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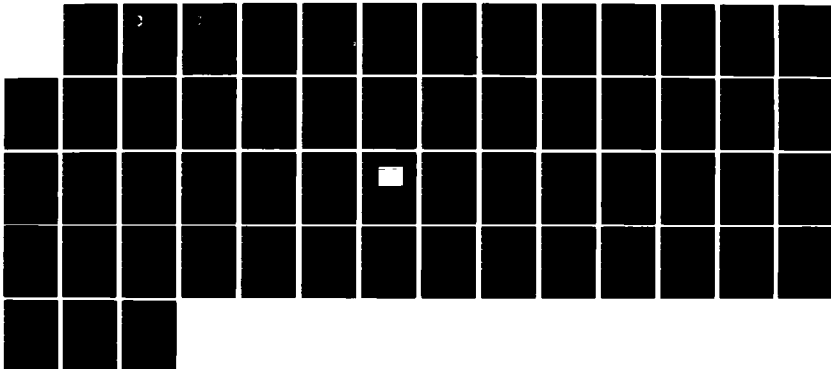
DEVELOPMENT OF A PLANAR HETEROJUNCTION BIPOLAR  
TRANSISTOR FOR VERY HIGH S. (U) CALIFORNIA UNIV SANTA  
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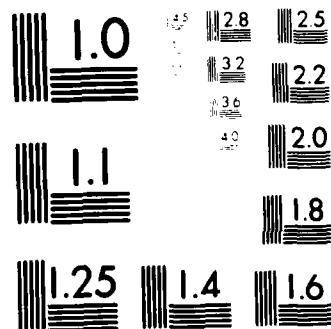
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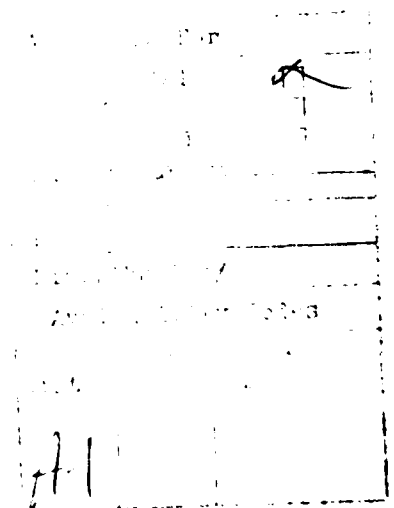
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Development of a Planar Heterojunction Bipolar  
Transistor for Very High Speed Logic

Stephen I. Long, Herbert Kroemer and M.A. Rao  
University of California  
Department of Electrical & Computer Engineering  
Santa Barbara, CA 93106

ABSTRACT

The following report describes the results of research on III-V molecular beam epitaxial (MBE) growth, material characterization and the fabrication of heterostructure bipolar transistors (HBT) for very-high-speed logic applications. During the reporting period work on the InGaP/GaAs heterojunction (HJ) was completed. Isotype HJs were grown and evaluated by a CV reconstruction method in order to determine the energy band offsets. It was found that  $\Delta E_c = 0.21$  eV and  $\Delta E_v = 0.25$  eV for the lattice matched composition. A new direction toward improvement in performance and fabrication techniques for the AlGaAs/GaAs HBT was successfully demonstrated. Graded-bandgap nonalloyed ohmic contacts using n+ InAs for the AlGaAs emitter and p+ GaSb for the GaAs base were provided by selective epitaxial regrowth. The MBE growth conditions for grading from GaAs to InAs and GaAs to GaSb were determined. Low specific contact resistances were observed for both contact types. A AlGaAs/GaAs graded-gap contact HBT was grown. A current gain of 20 was measured with only simple wire probes on the base and emitter.



## 1. INTRODUCTION

The following report presents a summary of the research results from the project "Development of a planar heterojunction bipolar transistor for very high speed logic" over the interval from October 1, 1984 to March 1, 1986.

During this period, work on the inverted GaAs/AlGaAs Heterostructure Bipolar Transistor (HBT) was completed and documented by a Ph.D. dissertation [1]. One result of this task was to develop an improved technique for evaluation of the base spreading resistance in HBT structures, a major parasitic element which degrades the performance. In addition, a non-intentionally doped, graded region between emitter and base was shown to provide an improved transition between the wide gap emitter and narrow gap base eliminating the conduction band spike and providing a buffer for Be diffusion. Copies of this dissertation were provided to AFOSR in Oct. 1985. Further activity on the inverted HBT was determined to be unnecessary due to the very rapid progress being made on GaAs/AlGaAs HBTs for digital and analog circuits in industrial laboratories [2, 3].

Research on the MBE growth and characterization of InGaP/GaAs heterojunctions and HBTs was also completed during the above time period. Techniques were developed for growth of lattice-matched InGaP/GaAs heterojunctions which requires very careful control of the group III flux ratios and the  $P_2$  flux. The emphasis on this task was shifted from HBT fabrication (preliminary work had led to successful results at UCSB [4]) to growth of N-n and P-p isotype heterojunctions for the accurate evaluation of the energy band lineups. The reason for the change in direction was due to the discovery in 1984 [5] that the AlGaAs/GaAs HJ did not have the undesireably high conduction band offset and small valence band offset which had been predicted and experimentally justified in the late 70's. While InGaP/GaAs was theoretically predicted to have a much more favorable lineup for HBT purposes, no experimental data existed to verify the theory which was by that time under suspicion of being inaccurate. Before further work on InGaP/GaAs HBTs could be justified, the accurate measurement of the energy band lineups must be carried out. This was done at UCSB by a C-V technique, and the results are reported in section 2 and appendix



A of this report. In addition, an MS dissertation is also in preparation. The result provided new and useful information, but also confirmed that further efforts on InGaP/GaAs HBTs were not justifiable due to the much greater difficulty in MBE growth when compared with the AlGaAs/GaAs system. The InGaP/AlGaAs system does, however, look interesting for optoelectronic device applications.

A new direction toward improvement in performance and fabrication techniques for the AlGaAs/GaAs HBT was successfully established and was shown to be highly promising during late 1985/early 1986. Since the contacts to the device are highly critical in achieving the theoretical performance of the HBT, an alternative to the Au/Ge/Ni and Au/Zn "ohmic" contact systems has been evaluated. This new approach utilizes a graded transition between  $n^+$ -AlGaAs and  $n^+$ -InAs for n type contacts and  $p^+$ -GaAs to  $p^+$ -GaSb for p type contacts. It is well known that the Fermi level in n-InAs is pinned inside the InAs conduction band. Not as well known is the similar property for p-GaSb, that is the Fermi level is pinned in the valence band. Therefore, nonalloyed ohmic contacts will be possible on both material systems. Nonalloyed contacts are desirable because the alloying process causes penetration of the metal regions into the semiconductor. This penetration must be allowed for in the design of an emitter structure, for example, which forces the thickness to be larger than desirable for best performance. In addition, the nonalloyed contact will allow the same metal to be used for both p and n type contacts, opening up the possibility for self-aligned structures.

Preliminary results have been very encouraging, with specific contact resistances of  $5 \cdot 10^{-8} \Omega\text{-cm}^2$  being observed on n-type transitions and  $3 \cdot 10^{-6} \Omega\text{-cm}^2$  on p-type transitions. In addition, an HBT device with graded-gap base and emitter contacts was grown by a selective regrowth technique, fabricated, and demonstrated to have a current gain of 20 when contacted only by tungsten wire probes (no metallization at all). Details on this work are reported in sections 3 and 4 of this report. Appendix A also contains a preprint of a paper in which a graded-gap contacted MESFET was demonstrated in the UCSB laboratory under SRC funding.

## 1.1 FUTURE PLANS

Work will continue on the graded-gap contacted HBT under a no-cost extension to this project. Efforts will be made to optimize the growth procedure and graded structure for minimum contact resistance and to work toward the achievement of a high-performance self-aligned HBT using nonalloyed metal or silicide contacts.

## 1.2 PERSONNEL

Research assistants M. Rao and B. Hancock were supported by this contract during the reporting period. Mr. Hancock completed his Ph.D. dissertation in June 1985. Mr. Rao is completing an MS dissertation on InGaP MBE growth and characterization, and is working on the graded-gap HBT. The work was supervised by Profs. S. Long and H. Kroemer, co-principal investigators.

## 1.3 REFERENCES

- [1] B. Hancock, "Development of inverted (Al,Ga)As heterojunction bipolar transistors by molecular beam epitaxy", Ph.D. dissertation, University of California, Santa Barbara, June 1985.
- [2] P. Asbeck, et al., "Application of HBTs to High Speed Small-Scale Digital ICs", 1984 GaAs IC Symposium Proceedings, pp. 133-136.
- [3] T. Ohshima, et al., "A Self-Aligned GaAs/AlGaAs HBT with V groove isolated planar Structure", 1985 GaAs IC Symposium Proceedings, pp. 53-56.
- [4] M. J. Mondry and H. Kroemer, "Heterojunction bipolar transistor using a (Ga,In)P emitter on a GaAs base, grown by molecular beam epitaxy," IEEE Elect. Dev. Lett. EDL-6 (#4), pp. 175-177, April 1985.
- [5] H. Kroemer, "Band offsets at heterointerfaces: theoretical basis, and review, of recent experimental work," Proc. 2nd Int. Conf. Modulated Semiconductor Structures, (MSS-II), Kyoto, 1985.

## 2. MOLECULAR-BEAM EPITAXIAL GROWTH OF (Ga,In)P/GaAs HETEROSTRUCTURES

During 1985, this project underwent a major change in direction, from an attempt to build a heterostructure bipolar transistor with a (Ga,In)P emitter on a GaAs base-and-collector structure, to an accurate determination of the energy band lineup at (Ga,In)P/GaAs heterojunctions (HJs). The reasons for this change were as follows. It may be recalled that the original motivation for the investigation of the (Ga,In)P/GaAs heterostructure system was the desire to obtain a more optimal band lineup in heterostructure bipolar transistors (HBTs). Ideally, the conduction band offset at an (abrupt) emitter-base junction in a HBT should be as small as possible, with a large valence band offset. The band lineups in the almost-universally-used (Al,Ga)As/GaAs system, as they had been determined experimentally during the late-70's, exhibited an undesirably large conduction band offset (typically, for 30% Al, 0.32 eV) and a corresponding undesirably small valence band offset (typically 0.06 eV). To obliterate the resulting undesirable conduction band spike barrier, the emitter-base junction was compositionally graded, which is technologically complex, and which appeared to introduce defects at the interface. These, in turn, were suspected to be at least partially responsible for the fact that HBTs have so far never lived up to their theoretical performance potential, even if the emitter-base junction was graded. It had been predicted theoretically [1] that the (Ga,In)P/GaAs HJ would have a much more desirable band lineup, with a smaller conduction band offset (0.16 eV) and a much larger valence band offset (0.29 eV). During 1984, the first such transistors had been constructed under a University of California MICRO project [2].

During the second half of 1984, the then widely accepted experimental data for the band lineups in the (Al,Ga)As/GaAs system suddenly came under suspicion, and by early-1985 there could no longer be any doubt that the conduction band offsets in the (Al,Ga)As/GaAs system were significantly smaller (typically 0.25 eV) [3] and hence much less unfavorable for HBTs than had been believed. This reduced somewhat the incentive for the development of an alternate (Ga,In)P/GaAs technology, especially in the face of our experience, gained during 1983 and 1984.

that such a technology was far more difficult than had been believed on the basis of our earlier very favorable experiences with straight GaP, as opposed to (Ga,In)P. Finally, the revision of the band lineups in the (Al,Ga)As/GaAs system [3] raised serious doubts about the validity of the theoretical predictions for the band lineups in the (Ga,In)P/GaAs system: These prediction had been based on Harrison's theory of band lineups [4], which until 1984 had been widely accepted as being remarkably reliable. It turned out that the revised band lineups in the (Al,Ga)As/GaAs system were in flagrant contradiction to that theory, thus destroying the credibility of that theory also for other hetero-systems.

This combination of circumstances called for an experimental determination of the band lineups in the (Ga,In)P/GaAs system, before continuing the development of the difficult technology for that system. This determination was undertaken and successfully completed during 1985.

The method employed was capacitance-voltage (C-V) profiling, introduced as a technique for determining band offsets at hetero-interfaces by Kroemer et al. [5-7]. This technique has a number of attractive features. For one, it is insensitive to compositional grading (but not to doping gradients!) across the interface [6]. Also, it provides a means of independently determining the valence band edge discontinuity  $\Delta E_v$  and the conduction band discontinuity  $\Delta E_c$ , in separate measurements. A self-consistency check is therefore obtained if the values of the two discontinuities add up to the known energy gap difference  $\Delta E_g$  between the two materials. Finally, a powerful additional self-consistency check may be performed, through the use of computer reconstruction of what should have been the experimental C-V profile for the particular band offset data found, and comparison of that reconstructed profile with the experimental one.

## 2.1 SAMPLE STRUCTURES

Epitaxial layers of (Ga,In)P and GaAs were grown by molecular beam epitaxy in a Varian-360 MBE machine, on (100)-oriented, Si-doped n+ GaAs substrates. Both n-n and p-p isotype structures were grown, for separate  $\Delta E_c$  and  $\Delta E_v$  measurements. With the n-n structures, the

profiling was conducted from a reverse-biased aluminum Schottky barrier deposited on the n-(Ga,In)P surface. Because Schottky barriers on p-(Ga,In)P were too leaky to permit C-V profiling, the profiling of the p-p HJs was carried out by profiling upward from the reverse-biased  $n^+$ -p junction between the  $n^+$  substrate and the p-GaAs epi-layer.

One of the central problems in the MBE growth of ternary alloy semiconductors is the achievement of an alloy composition with good lattice match at the HJ. This requires a careful control of the Ga:In flux ratio. As described last year, our nude ion gauge beam flux monitor was found to be insufficiently reproducible to obtain the desired lattice match reliably. Therefore, X-ray diffractometer data were taken on all layers grown, and layers with unsatisfactory lattice match were discarded. On our best n-n sample, diffractometry indicated that the (Ga,In)P epi-layer was slightly Ga-rich, with a relative lattice mismatch of approximately  $10^{-3}$ , while on our best p-p sample a much smaller relative lattice mismatch of less than  $10^{-4}$  was achieved.

## 2.2 C-V PROFILING: RESULTS AND DISCUSSION

Because we found the p-p results more trustworthy, they are discussed first.

### 2.2.1 $\Delta E_v$ MEASUREMENTS

As stated earlier, the C-V profile through the p-(Ga,In)P/p-GaAs HJ was obtained by reverse biasing the  $n^+$ -p junction between the substrate and the p-GaAs epi-layer. The apparent majority carrier concentration profile  $p(x)$  of Fig. 2.1 was obtained.

From this profile we calculate  $\Delta E_v = 0.239$  eV. The reconstructed profile is also shown in Fig. 2.1. It can be seen that the agreement between the experimental and reconstructed profiles, although far from perfect, is quite good. The remaining discrepancies must be viewed as indications that our model of a perfectly abrupt interface is not fully applicable, but it is difficult to say more. Expressed as a fraction of the total energy gap difference,  $\Delta E_g \approx 0.459$  eV [8], our  $\Delta E_v$ -value corresponds to  $0.52 \Delta E_g$ .

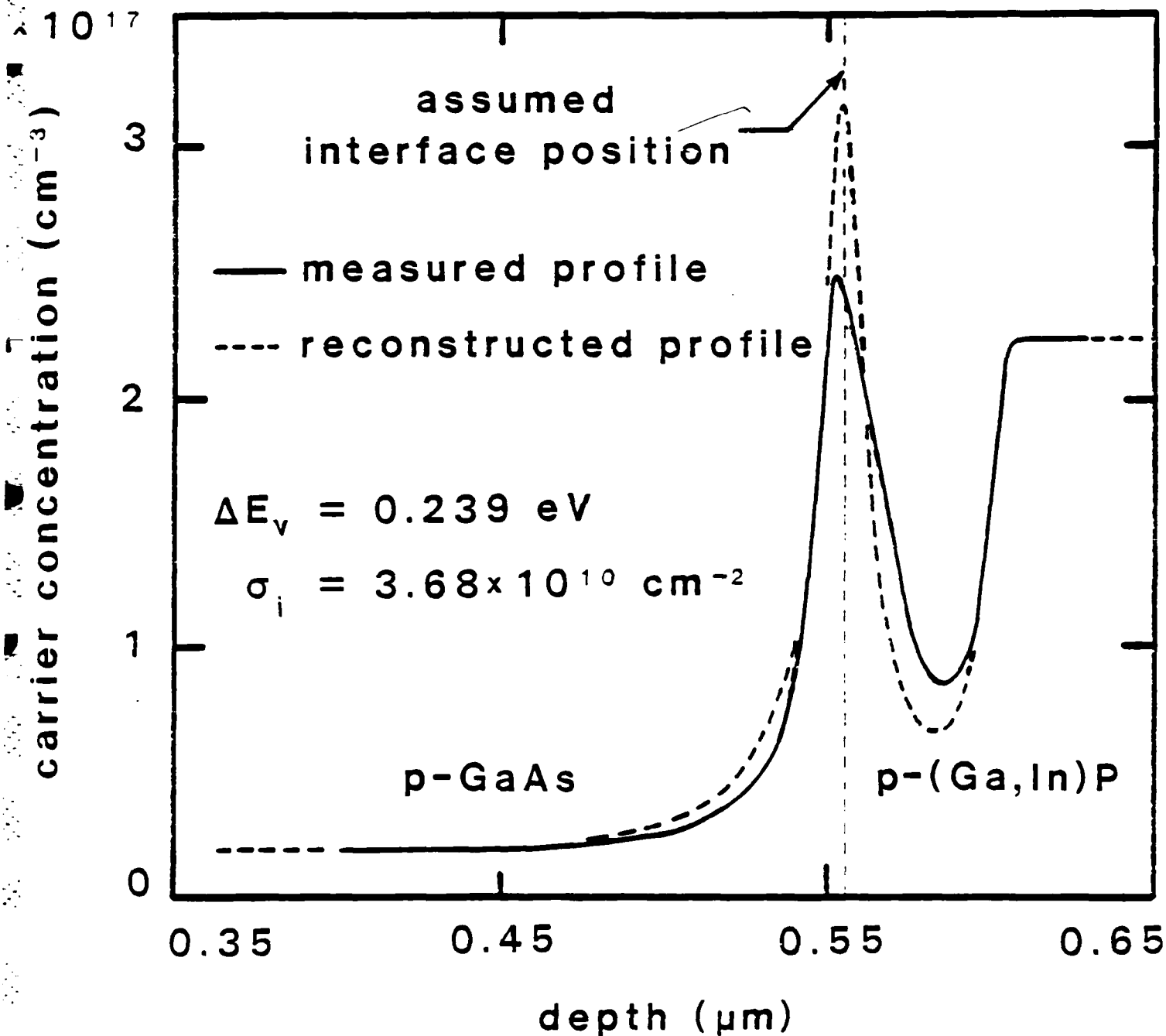


Fig. 2.1 Experimental and reconstructed (apparent) carrier concentration profile for the p-p heterojunction.

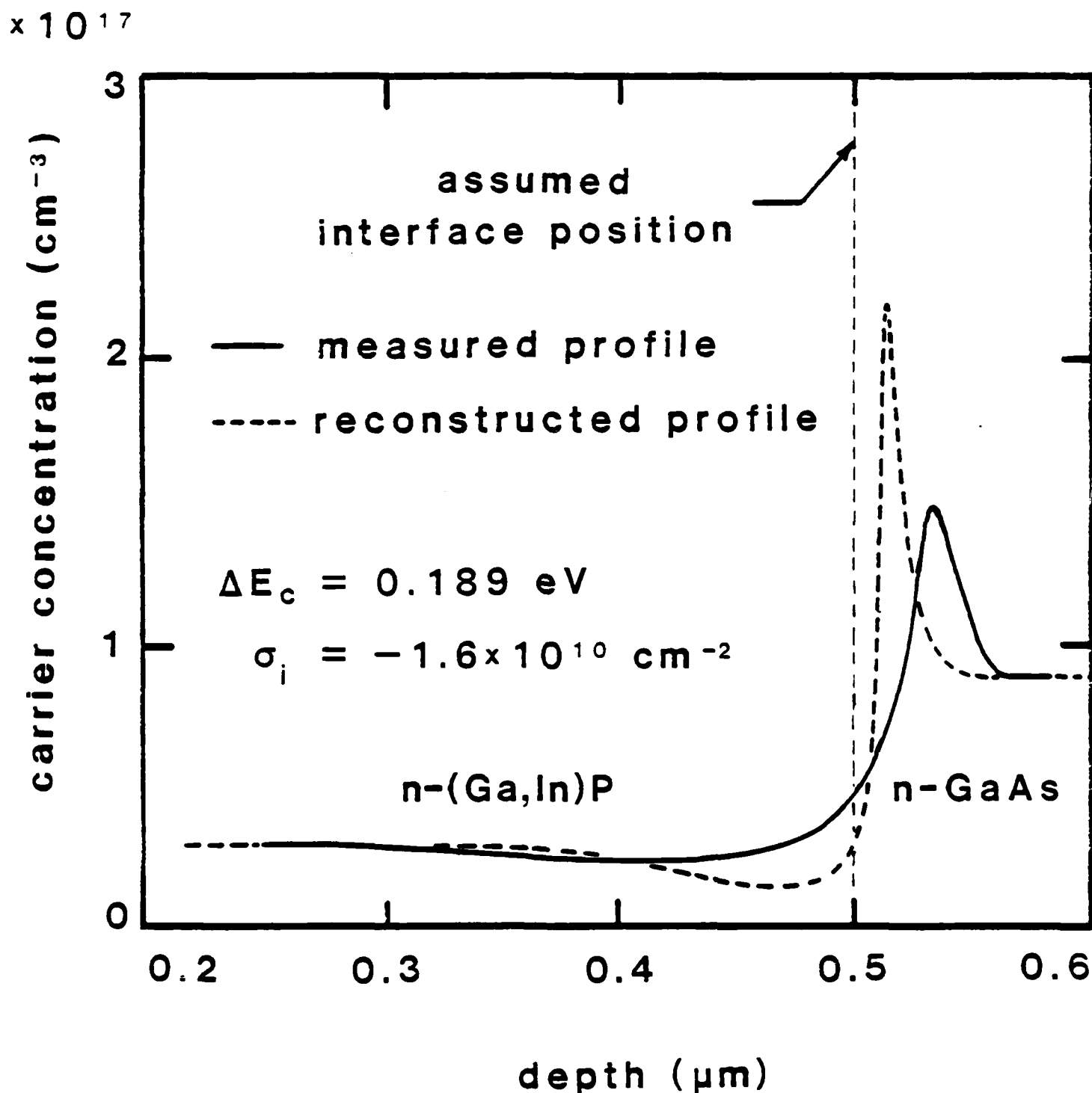


Fig. 2.2

Experimental and reconstructed (apparent) carrier concentration profile for the n-n heterojunction. The value of  $\Delta E_c$  is the value before applying corrections for graded doping.

Our experimental value is about 50 meV smaller than the theoretical prediction [1] of  $\Delta E_v \approx 0.29 \text{ eV} \approx 0.65 \Delta E_g$  for the lattice-matched (Ga,In)P/GaAs interface, obtained by simple linear interpolation between the theoretical valence band offsets for GaP/GaAs and InP/GaAs that are predicted by the Harrison theory [4]. Although by no means negligible, this discrepancy is actually smaller than the discrepancy for most hetero-systems. Unfortunately, however, it is a change in the direction undesirable for HBTs.

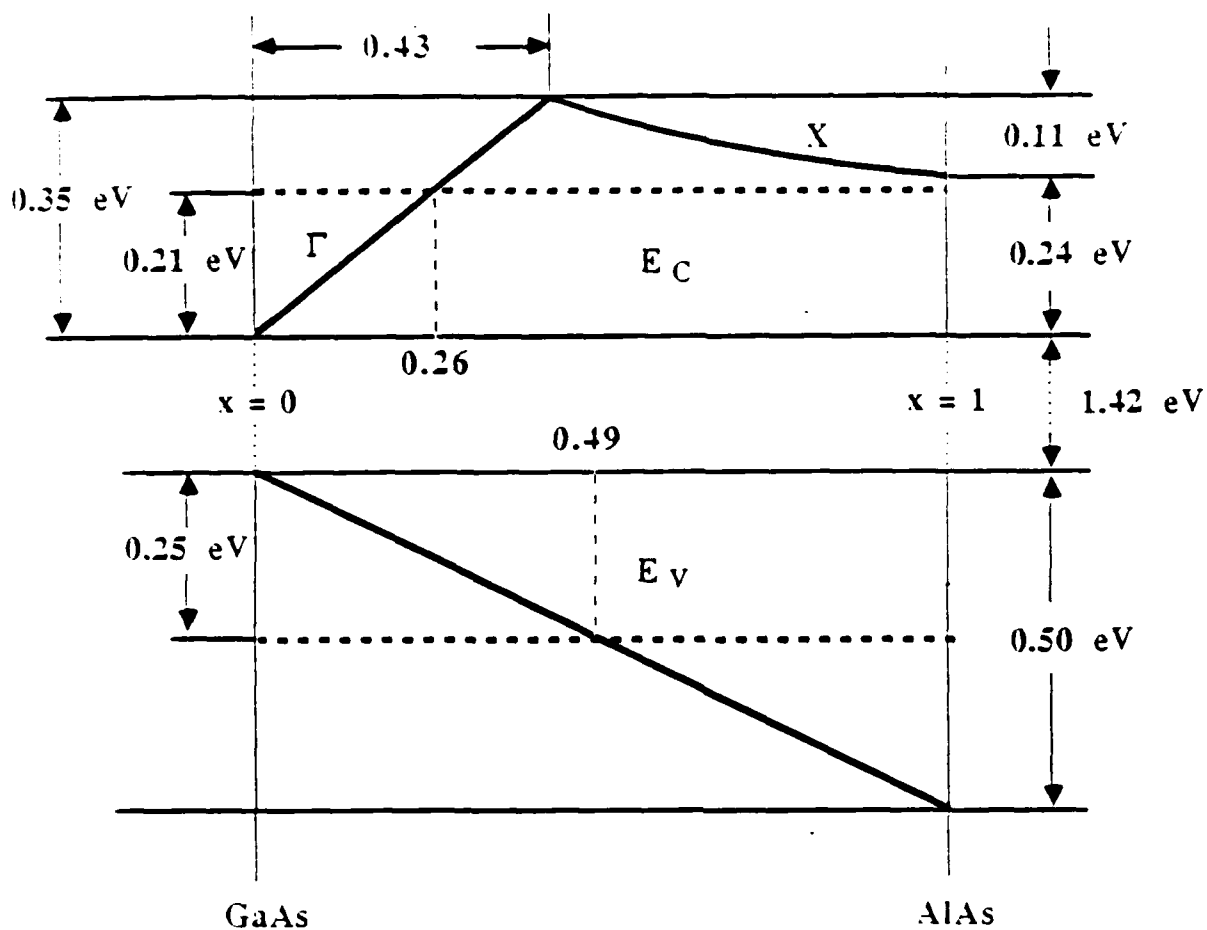
### 2.2.2 $\Delta E_c$ MEASUREMENTS

To measure  $\Delta E_c$ , an aluminum Schottky barrier deposited on the top (Ga,In)P epitaxial layer was reverse-biased to obtain a C-V profile through the HJ. Fig. 2.2 shows the experimental carrier concentration profile, in which electron accumulation and depletion can be seen in the GaAs and (Ga,In)P, as expected. The conduction band offset obtained from this profile is  $\Delta E_c = 0.189 \text{ eV}$ .

We were not able to obtain as good a fit between experimental and reconstructed carrier concentration profiles as for the p-p case. The reconstructed profile in Fig. 2.2 shows that the peak-to-valley concentration ratio of the experimental profile is lower, and the peak and valley are separated farther in space than in the reconstructed profile. This combination indicates that either the energy gap or the doping profile of the actual junction must be graded at the transition, in contrast to the mathematical model used in the reconstruction, which assumed an abrupt transition at the interface for both.

The difference between the two kinds of gradients is important for the determination of the band offset: As was shown by one of us [6], in the presence of a purely compositional (energy gap) gradient at the HJ, not accompanied by a doping gradient, the electrostatic dipole moment associated with the broadened  $n(x)$  curve remains unchanged, and the standard interpretation of the C-V data still yields the correct (abrupt-limit) value of  $\Delta E_c$ , even though the reconstruction with an abrupt mathematical model fails. On the other hand, if the doping profile is graded, this changes the dipole moment, and hence the band offset.





**Fig. 2.3** Predicted relative band edge energies at  $(\text{Ga,In})\text{P}/(\text{Al,Ga})\text{As}$  heterojunctions. The heavy solid lines represent the band energies in the  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  alloy system, relative to straight GaAs, as a function of  $x$ , taken from ref. 3. The horizontal broken lines represent the  $(\text{Ga,In})\text{P}$  band energies relative to GaAs, for  $(\text{Ga,In})\text{P}$  lattice-matched to GaAs, as determined in the present work.

A sputter-Auger analysis of our sample, which would have been able to detect any compositional grading on the scale required by the discrepancy between the two curves in Fig. 2, showed no significant compositional grading near the HJ. We therefore concluded that in our case the grading is due to a doping gradient rather than a compositional gradient. We suspect that the postulated doping gradient is due to strain-induced diffusion: In our n-n sample, significant outdiffusion of Si probably has taken place at the GaAs/(Ga,In)P interface, due to strain caused by the non-negligible residual lattice mismatch in that sample. In contrast, it should be recalled that the p-p isotype interface was relatively strain-free.

If one inspects the theory, one finds readily that the presence of a doping gradient at the interface causes an increase in the value of  $\Delta E_c$  relative to the abrupt-model value. We estimate the correction to be 0.024 eV, yielding a corrected conduction band offset of  $\Delta E_c \approx 0.213 \text{ eV} \approx 0.46 \Delta E_g$ . The value of  $\Delta E_c$  predicted from the Harrison model was  $0.160 \text{ eV} \approx 0.35 \Delta E_g$ .

Our two independent experimental band offsets add up to  $\Delta E_v + \Delta E_c = 0.452 \text{ eV}$ , less than 2% below the experimental value of the energy gap difference,  $\Delta E_g = 0.459 \text{ eV}$ , suggesting that the individual values should be quite trustworthy. The remaining discrepancy of 7 meV probably reflects a small amount of doping grading at the p-p interface. Inasmuch as our reconstruction fit for the p-p junction is distinctly less than perfect, we assign the discrepancy to the valence band offset, implying an adjusted value  $\Delta E_v \approx 0.246 \text{ eV} \approx 0.54 \Delta E_g$ .

### 2.3 CONCLUSIONS

The valence and conduction band edge discontinuities for (Ga,In)P lattice-matched to GaAs have been determined by C-V profiling. We find a conduction band offset of 0.21 eV, only slightly smaller than the typical value of 0.25 eV obtained in the  $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$  system for  $x = 0.3$ . Together with the more difficult technology of (Ga,In)P relative to (Al,Ga)As, the closeness of the two values eliminates the incentive for (Ga,In)P as a material for HBTs, and we have, in fact, terminated work towards such a device. The material remains of great interest, however, for

optoelectronic device structures. In fact, our band lineup data provide a long-missing quantitative basis for the design of such devices.

Our data lead to interesting predictions for the band lineups for (Ga,In)P lattice-matched to  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ . In Fig. 2.3, taken from a recent review [3], we have superimposed our conduction and valence band edge energy values for (Ga,In)P on current "best estimate values" for the lineups within the  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  alloy system [3]. It appears that the valence band of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  will drop below that of lattice-matched (Ga,In)P for  $x > 0.49$ . The conduction band offsets are more complicated, due to the  $\Gamma$  - to - X crossover in the  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  band structure around  $x = 0.43$ . We estimate that the conduction band of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  will initially rise above that of (Ga,In)P for  $x > 0.26$ . For  $x > 0.43$ , the conduction band energy of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  drops again, and it should reach a value very close to the (Ga,In)P value as  $x$  approaches 1.0. Thus there are likely to be three  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  composition ranges with quite different behavior: (i) For  $x < 0.26$ , the band lineup should remain a straddling one, with  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  retaining the lower total gap, and with a vanishing conduction band offset at the upper end of this range. (ii) For  $0.26 < x < 0.49$ , the system should be a staggered one, with (Ga,In)P having both bands below those of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ . The residual interface gap should slowly increase through this range, from about 1.77 eV for  $x = 0.26$  to 1.95 eV for  $x = 0.49$ . This might be an interesting range for the study of staggered-lineup luminescence [9],[10] at p- $\text{Al}_x\text{Ga}_{1-x}\text{As}$ /n-(Ga,In)P heterojunctions. (iii) For  $x > 0.49$ , the band lineup would become straddling again, but now with (Ga,In)P having the smaller energy gap.

## 2.4 ACKNOWLEDGMENTS

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## 2.5 REFERENCES

- [1] H. Kroemer, "Heterostructure bipolar transistors : What should we build ?," J. Vac. Sci. Technol. **B1** (#2), pp.126-130 Apr.-June 1983.
- [2] M. J. Mondry and H. Kroemer, "Heterojunction bipolar transistor using a (Ga,In)P emitter on a GaAs base, grown by molecular beam epitaxy," IEEE Electron Dev. Lett. **EDL-6** (#4), pp. 175-177, April 1985.
- [3] For a review containing extensive references to the original workers, see H. Kroemer, Proc. 2nd Int. Conf. Modulated Semicond. Structures, (MSS-II), Kyoto, 1985; Surf. Sci., in print.
- [4] W. A. Harrison, "Elementary theory of heterojunctions," J. Vac. Sci. Technol. **14** (#4), pp. 1016-1021, July/Aug 1977.
- [5] H. Kroemer, W. Y. Chien, J. S. Harris, Jr., and D. D. Edwall, "Measurement of isotype heterojunction barriers by C-V profiling," Appl. Phys. Lett. **36** (#4), pp. 295-297, Feb. 1980.
- [6] H. Kroemer, "Determination of heterojunction band offsets by capacitance-voltage profiling through nonabrupt isotype heterojunctions," Appl. Phys. Lett. **46** (#5), pp. 504-505, March 1985.
- [7] D. Babic and H. Kroemer, Solid-State Electron. **28**, 1015 (1985).
- [8] H. C. Casey, Jr. and M. B. Panish, *Heterostructure Lasers Part B: Materials and Operating Characteristics* ( Academic, New York, 1978), see Table 5.3-1.
- [9] H. Kroemer and G. Griffiths, IEEE Electron Dev. Lett. **EDL-4**, 20 (1983).
- [10] E. J. Caine, S. Subbanna, H. Kroemer, J. L. Merz, and A. Y. Cho, Appl. Phys. Lett. **45**, 1123 (1984).

## 2.6 PUBLICATIONS

A paper on the subject of this report, but of much greater length, has been submitted to the Journal of Applied Physics, and is reproduced in Appendix A.

### 3. NON-ALLOYED GRADED-GAP OHMIC CONTACTS TO n AND p-type GaAs

One of the most troublesome areas of all compound semiconductor technology is that of the (so-called) ohmic contacts. The poorly understood and poorly reproducible Au/Ge/Ni and Au/Zn alloy contacts to n and p-type GaAs respectively, are rapidly emerging as severe limitations on the further progress of compound semiconductor devices.

#### 3.1 THE (Ga,In)As n-type CONTACT

In 1981 Woodall et al. [1] proposed and demonstrated a non-alloyed graded-gap scheme for obtaining ohmic contacts to n-type GaAs, by first growing a graded transition from GaAs to InAs and then making a non-alloyed metallic contact to the InAs. It is well known that at a metal-to-InAs interface the Fermi level is pinned inside the InAs conduction band [2], hence this interface by itself acts as an ideal negative-barrier ohmic contact. However, if the GaAs-to-InAs transition were not graded, it would act as a quasi-Schottky barrier with a barrier height close to the conduction band offset  $\Delta E_c$  of the GaAs/InAs heterojunction, about 0.9eV [3], and the contact would be poor overall. Sufficient grading obliterates the heterojunction barrier, and leads to an excellent ohmic contact with properties that can be superior to the traditional, widely-used Au-Ge/Ni/Au alloyed system [4-6]. In fact, it is probably not necessary to grade all the way to InAs: Kajiyama et al. [7] have shown that a zero or negative surface barrier height exists for In:Ga ratios above 80:20. The band diagram for an abrupt GaAs/InAs interface and that for a graded GaAs/InAs interface is shown in Fig. 3.1.

In their work, Woodall et al. [1] graded over a rather large distance, about 2500Å. For a negative surface barrier height, the series resistance of the graded transition region should be the dominant residual contribution to the contact resistance. This suggests using a graded region no longer than necessary for flattening out the bands. The necessary grading may be estimated as follows. If the transition region is graded over a width  $w$ , the graded offset is equivalent to an electric field  $\mathcal{E}_Q = \Delta E_c / qw$ . This quasielectric field must be compensated by a true electric field, which must be supported by charges near the ends of the graded region. To insure a flat conduction band, the doping level must be sufficiently high to make it possible to support this field with the donors contained in a region significantly thinner than the graded region itself. If  $N_D$  is the doping level and  $\epsilon$  the permittivity of the semiconductor, this leads to the condition

$$q N_D w \gg \epsilon \mathcal{E}_Q = \epsilon \Delta E_c / qw, \text{ or } N_D w^2 \gg \epsilon \Delta E_c / q^2. \quad (1)$$

Inserting numbers ( $\epsilon \approx 14\epsilon_0$ ;  $\Delta E_c \approx 0.9\text{eV}$ ) yields, on the right-hand side,  $7 \cdot 10^6 \text{ cm}^{-1}$ . With

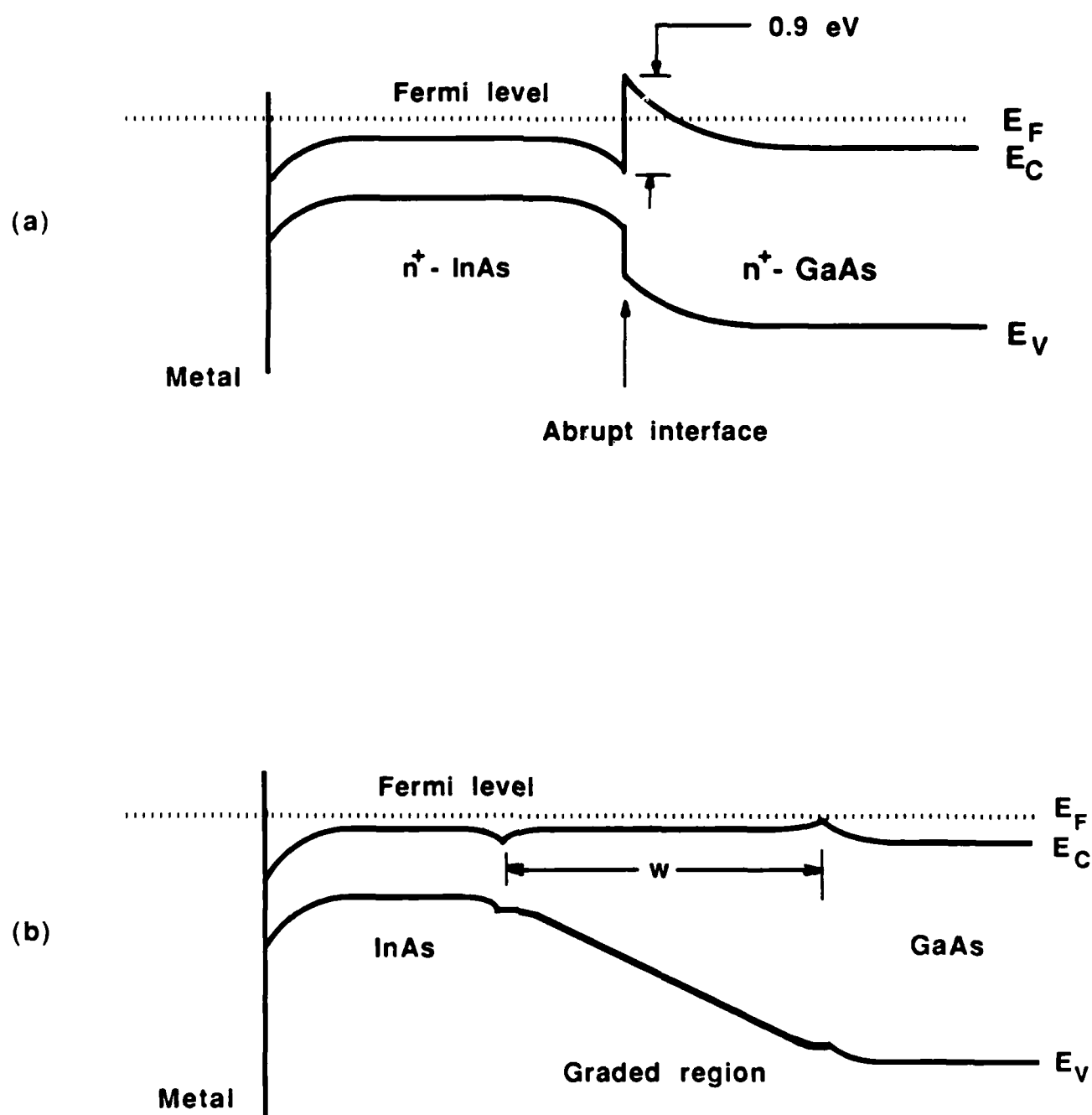


Fig. 3.1 Band Diagrams for (a) an abrupt GaAs/InAs interface, and (b) a graded GaAs/InAs interface

doping levels of  $1 \cdot 10^{19} \text{ cm}^{-3}$ , which have been demonstrated in GaAs [8], a more detailed analysis [9] shows that a safety margin of 10 is generous, corresponding to  $w \geq 2.6 \cdot 10^{-6} \text{ cm}$  as the required grading distance, about one-tenth the distance used by Woodall et al.

A doping level of  $10^{19} \text{ cm}^{-3}$  yields a resistivity below  $6 \cdot 10^{-3} \Omega\text{cm}$  [8]. For a 260 Å thick transition layer this corresponds to a contact resistivity below  $2 \cdot 10^{-9} \Omega\text{cm}^2$ . This value would be about a factor 35 below the lowest trustworthy value that has been reported for Au/Ge/Ni [6], and much lower than *typical* values for that system [5].

### 3.2 Ga(As,Sb) p-TYPE CONTACT

Analogously, at a metal-to-GaSb interface, the Fermi level is pinned inside the GaSb valence band, and hence the Ga(As,Sb) system would be suitable for p-type contacts. Band diagrams for the GaAs/GaSb system with and without grading are shown in Fig. 3.2. The theoretical analysis for the p-type graded-gap contact is similar to that for the n-type contact presented above in sec. 3.1. The theory predicts that contact resistivities below  $2 \cdot 10^{-8} \Omega\text{cm}^2$  should be possible for p-type contacts.

#### 3.2.1 GROWTH PROCEDURE

In order to grow the graded Ga(As,Sb) layer the Sb content should increase and the As content should decrease gradually over 250 Å, and at the surface the As content should be negligible. This grading can be achieved during MBE growth by controlling the arrival rates and sticking coefficients of the group V species by varying the substrate as well as the group V source temperatures. Chang et al [10] have determined the Sb content in Ga(As,Sb) layers as a function of the substrate temperature, the As/Ga flux ratio, and the Sb/Ga flux ratio. They find that the Sb content is negligible (less than 1% of the total group V species) when the substrate temperature is above 600°C and the As/Ga flux ratio is greater than 2. As the substrate temperature is lowered to about 470°C, the Sb content increases (to almost 90% of the group V

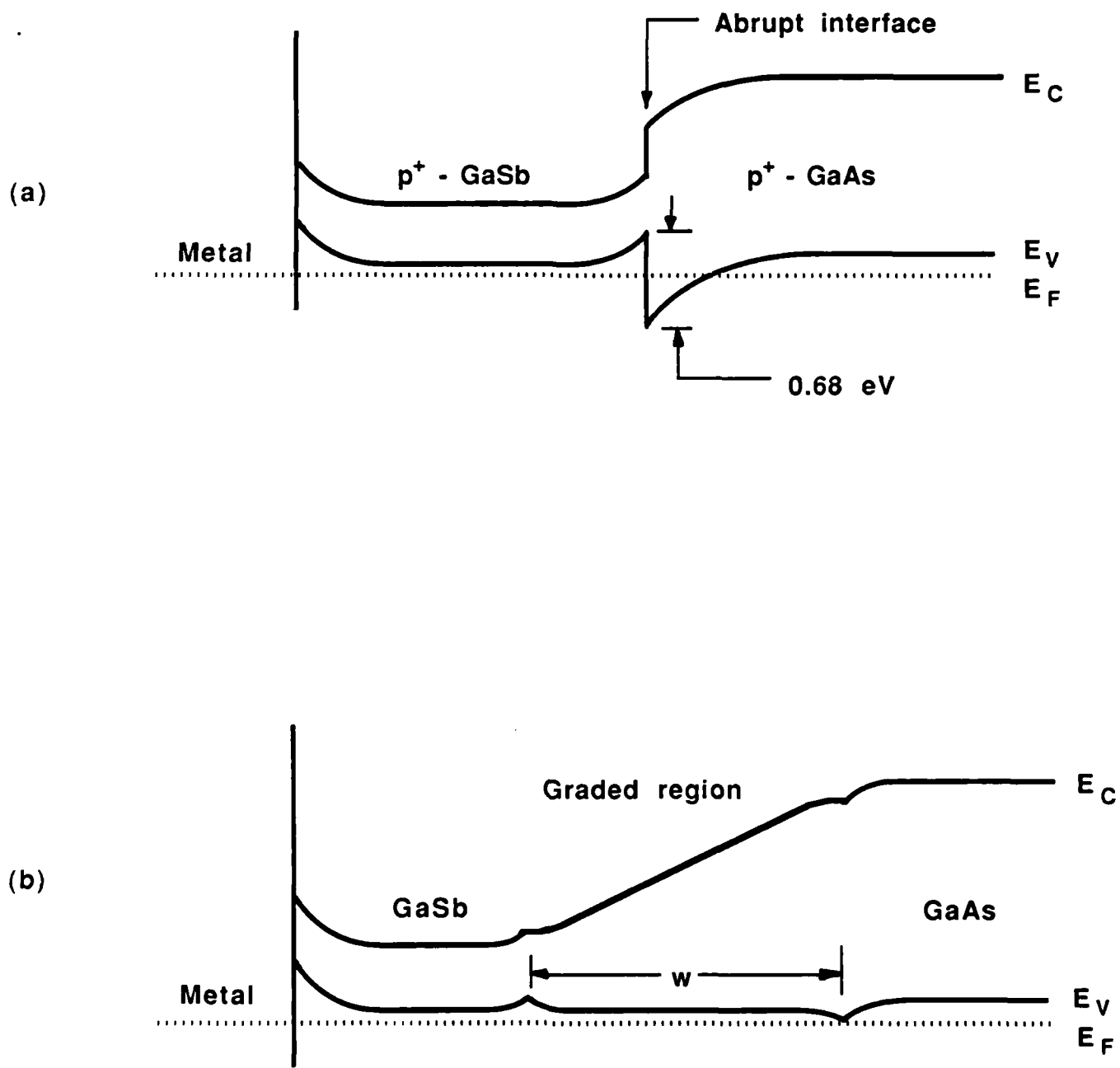


Fig. 3.2 Band diagrams for (a) an abrupt GaAs/GaSb interface, and (b) for a graded GaAs/GaSb interface



species), and is further enhanced as the As/Ga flux ratio drops below unity. A graphical representation of the variation in Sb content is reproduced from the work of Chang et al [10] in Fig. 3.3.

To develop a procedure for growing the Ga(As,Sb) transition regions the following experiment was performed.

Semi-insulating (100) LEC GaAs substrates were prepared by standard techniques prior to loading into a Varian-360 MBE machine. The native oxide was desorbed at 600°C in an As<sub>2</sub> background, at an *atomic* 2As<sub>2</sub>:Ga flux ratio ≤ 3:1. After a streaky 2 x 4 RHEED pattern was obtained, the structure shown in Fig. 3.4 was grown. The various layers and their functions are described below.

- (i) a 1500Å p<sup>+</sup>-GaAs buffer layer at a substrate temperature of 600°C, at a growth rate of 0.25µm/hr. Be was used as the p-type dopant.
- (ii) a 500Å Ga(As,Sb) layer at 600°C. The Sb/Ga flux ratio was 2:1. This layer was grown to provide information on Sb incorporation at 600°C in the presence of As<sub>2</sub> flux.
- (iii) a 400 Å Ga(As,Sb) layer with the substrate temperature being ramped down from 600°C to 470°C in a linear fashion. The As<sub>2</sub> and Sb fluxes were kept constant during this period. The purpose of this layer was to determine the Sb incorporation as a function of the substrate temperature.
- (iv) a 400Å Ga(As,Sb) layer during the growth of which the As<sub>2</sub> flux was decreased by turning off power to the As<sub>2</sub> source furnace at the start of the layer. The substrate temperature was kept constant at 470°C. This layer was grown to determine the Sb incorporation as a function of

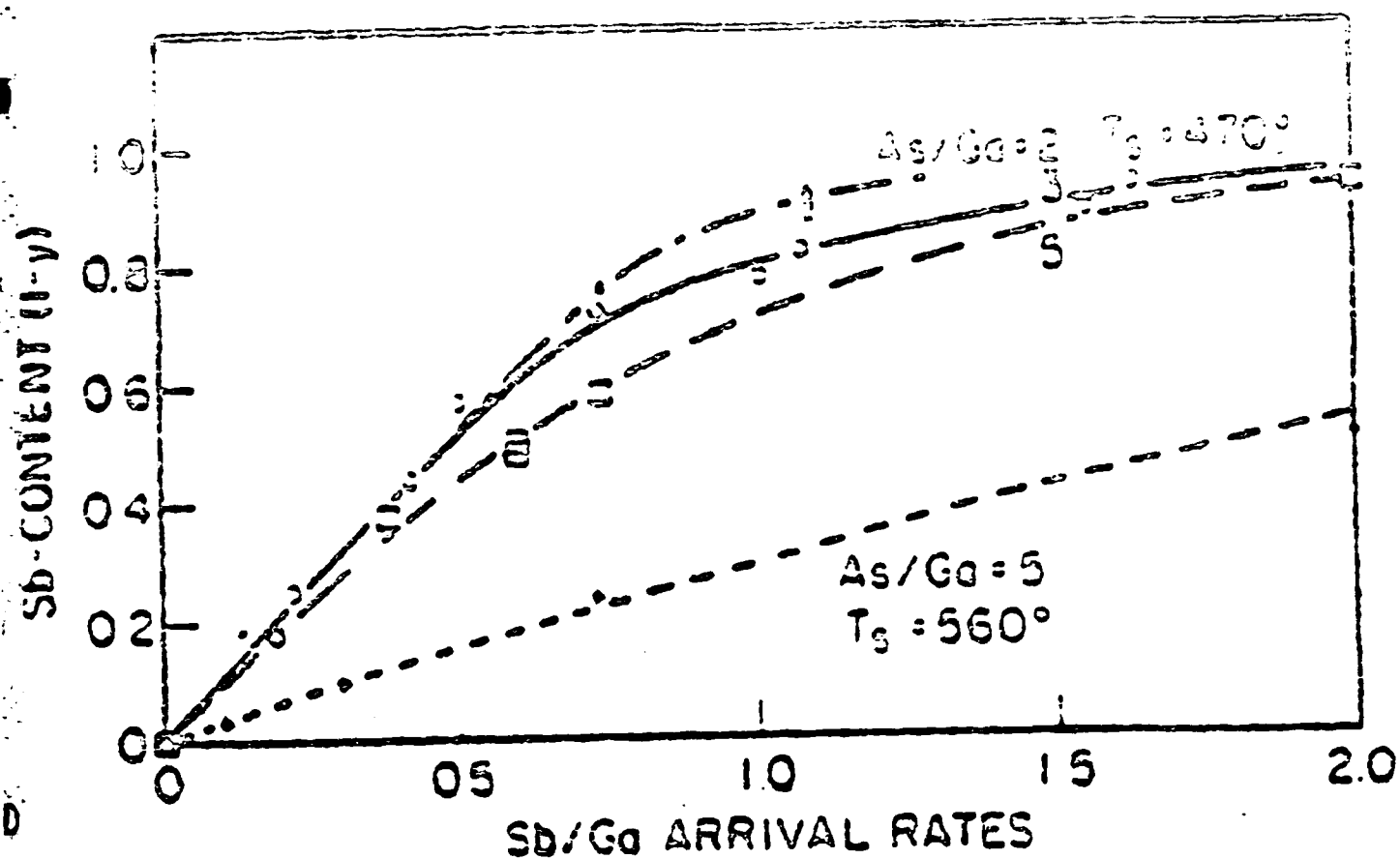


Fig. 3.3 Dependence of Sb content in the  $GaSb_{1-y}As_y$  films on the Sb arrival rate for various As arrival rates, which are normalized with respect to that of Ga. The substrate temperatures are indicated. Reproduced from [10].

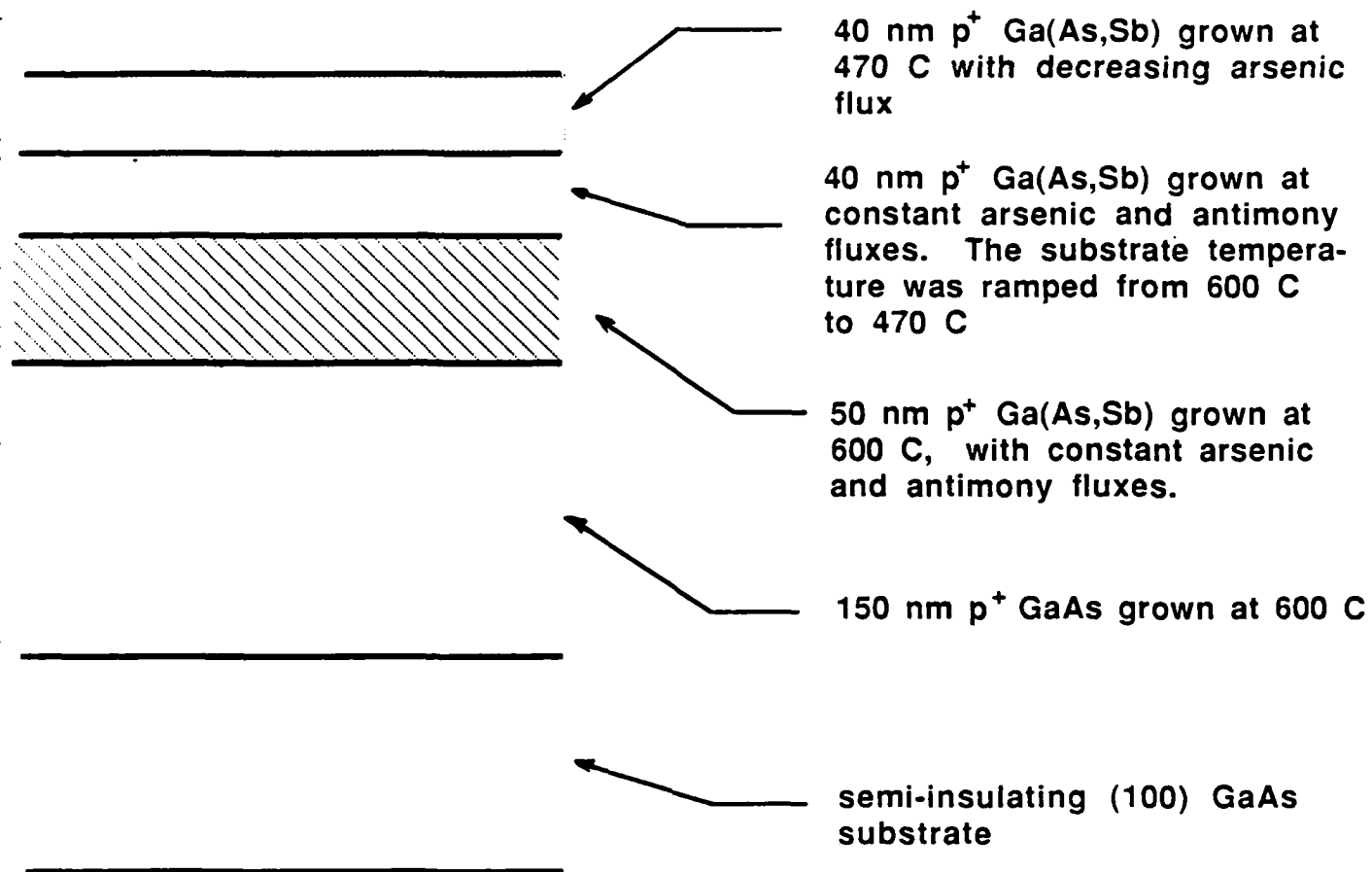


Fig. 3.4 Layer diagram for Ga(As,Sb) grading experiments. The structure shown above was grown by MBE.

decreasing  $\text{As}_2$  flux.

Layers (ii)-(iv) were also  $p^+$  doped, with a target hole concentration of  $10^{19} \text{ cm}^{-3}$

### 3.2.2. RESULTS

A sputter-Auger analysis of the sample described in sec.3.2.1 was performed. The atomic concentration versus distance profile so obtained is shown in Fig. 3.5. It can be seen that the Sb content for a depth  $> 800\text{\AA}$  (layer (ii) in sec. 3.1.1), is less than 3% of the group V species, thus showing that the Sb does not stick appreciably at  $600^\circ\text{C}$  in the presence of an  $\text{As}_2$  flux. The substrate temperature was ramped down from  $600^\circ\text{C}$  to  $470^\circ\text{C}$  for a depth between  $400\text{\AA}$  and  $800\text{\AA}$  (layer (iii)). In this layer the Sb concentration increases gradually to about 20%. In the first  $400\text{\AA}$  (layer(iv)), the Sb concentration increases to more than 90%, indicating that decreasing the  $\text{As}_2$  flux at  $470^\circ\text{C}$  is effective in grading the layer almost completely to GaSb. These results indicate that Ga(As,Sb) transition regions graded over  $\approx 300\text{\AA}$  can be grown by decreasing the substrate temperature linearly from  $600^\circ\text{C}$  to  $470^\circ\text{C}$  while reducing the  $\text{As}_2$  flux at the same time.

Contact resistivities were measured on the sample mentioned above using the Kelvin 4-terminal contact resistance measurement structures [11]. Cr/Au was used as the contact metal. Contact resistivities down to  $3 \cdot 10^{-6} \Omega \text{ cm}^2$  were measured, significantly better than typical for Au/Zn contacts. This value is still much higher than that predicted by a theoretical analysis, for two reasons. For one, the doping in the material turned out to be only about  $3 \cdot 10^{18} \text{ cm}^{-3}$ , and not  $1 \cdot 10^{19} \text{ cm}^{-3}$  as assumed in the analysis. For the other, the grading distance is  $800\text{\AA}$  and not  $250\text{\AA}$  as required by theory, in order to obtain contact resistivities in the  $10^{-8} \Omega \text{ cm}^2$  range. Such thin and highly doped graded layers are currently being grown, specifically for making contact resistance measurements. However, the graded-gap p-type contact has been already been incorporated in a heterostructure bipolar transistor (HBT), and this work is described in sec. 4.

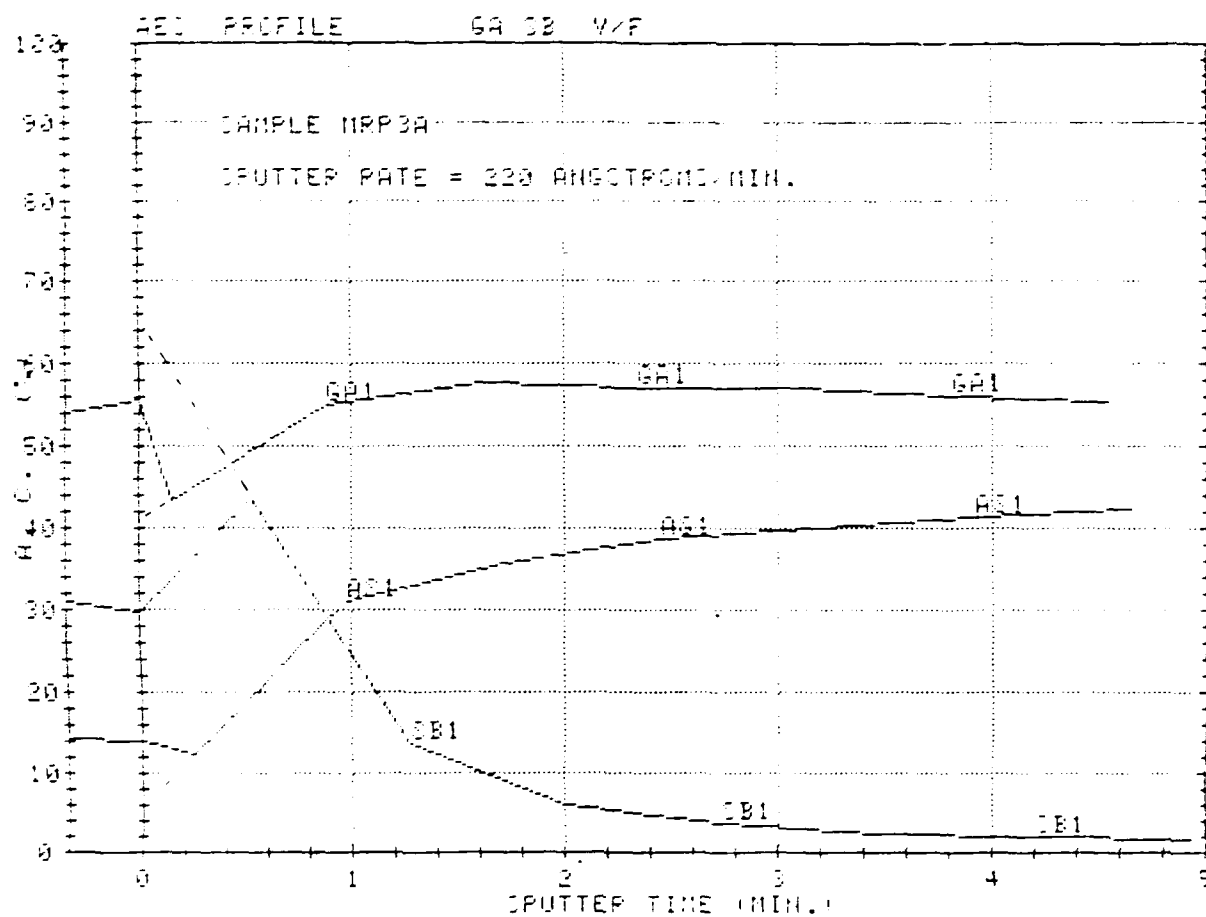


Fig. 3.5 Atomic concentration of Ga, As and Sb as a function of depth into the sample as determined by sputter-Auger analysis.

### 3.3 REFERENCES

- [1] J. M. Woodall, J. L. Freeouf, G. D. Pettit, T. Jackson, and P. Kirchner, "Ohmic contacts to n-GaAs using graded band gap layers of  $\text{Ga}_{1-x}\text{In}_x\text{As}$  grown by molecular beam epitaxy," *J. Vac. Sci. Technol.* **19**, 626 (1981).
- [2] C. A. Mead and W. G. Spitzer, "Fermi level position at metal-semiconductor interfaces," *Phys. Rev.* **134**, A713 (1964).
- [3] S. P. Kowalczyk, W. J. Schaeffer, E.A. Kraut, and R. W. Grant, "Determination of the InAs-GaAs (100) heterojunction band discontinuities by x-ray photoelectron spectroscopy (XPS)," *J. Vac. Sci. Technol.* **20**, 705 (1982).
- [4] T. Hara and T. Inada, "Trends in ion implantation in gallium arsenide," *Solid State Technol.* **22**, 69 (1979).
- [5] T. S. Kuan, P. E. Batson, T. N. Jackson, H. Rupprecht, and E. L. Wilkie, "Electron microscope studies of an alloyed Au/Ni/Au-Ge ohmic contact to GaAs," *J. Appl. Phys.* **54**, 6952 (1983).
- [6] A. A. Ketterson, F. Ponse, T. Henderson, J. Klem, C.-K. Peng, and H. Morkoc, "Characterization of extremely low contact resistances on modulation-doped FET's," *IEEE Trans. Electron Dev.* **ED-32**, 2257 (1985).
- [7] K. Kajiyama, Y. Mizushima and S. Sakata, "Schottky barrier height of n- $\text{In}_x\text{Ga}_{1-x}\text{As}$  diodes," *Appl. Phys. Lett.* **23**, 458 (1973).
- [8] See, for example: R. Sacks and H. Shen, "Highly doped GaAs:Si by molecular beam epitaxy," *Appl. Phys. Lett.* **47**, 374 (1985).
- [9] H. Kroemer, unpublished.
- [10] Chin-An Chang, R. Ludeke, L. L. Chang, and L. Esaki, "Molecular-beam epitaxy (MBE) of  $\text{In}_{1-x}\text{Ga}_x\text{As}$  and  $\text{GaSb}_{1-y}\text{As}_y$ ," *Appl. Phys. Lett.*, **31** (11), 759 (1977).
- [11] S. J. Proctor and L. W. Linholm, "A direct measurement of interfacial contact resistance," *IEEE El. Dev. Lett.*, **EDL-3** (10), 294 (1982).

#### 4. HETEROSTRUCTURE BIPOLAR TRANSISTOR WITH NON-ALLOYED BASE AND EMITTER CONTACTS

It was decided to incorporate the graded-gap contacts into n-p-n AlGaAs/GaAs heterostructure bipolar transistors (HBTs). The advantages of having graded-gap contacts in a HBT are first the greatly reduced base and emitter contact resistances over those possible with any conventional alloyed contacts. Besides, the graded-gap contacts are non-invasive. Therefore, thinner emitter structures will be possible since the  $\approx 1000\text{\AA}$  penetration depth of the alloyed contacts need not be added to the emitter region thickness. Finally, the base and emitter metallizations can be performed in one step.

##### 4.1 GROWTH PROCEDURE AND PROCESS DETAILS

The HBT structure shown in Fig. 4.1 was grown by MBE. The emitter-base junction was digitally graded as described by Su et al [1]. A  $500\text{\AA}$  Be diffusion setback layer was used in the base following the work of Malik et al [2] and B. Hancock [3]. A  $n^+$ -graded gap (Ga,In)As contact layer was grown above the emitter using the procedure developed by Dr. E. J. Caine in this laboratory [4]. This procedure is briefly described here. In order to grow the compositional transition region, the Ga flux should decrease and the In flux increase simultaneously in a complementary, roughly linear fashion. At a given initial growth rate, the lower limit of the width of a graded transition region is given by the rate at which the Ga flux from a Ga effusion cell drops if the power to the latter is simply turned off. After some experimentation with the flux transient dynamics of the Ga and In sources, the following growth schedule was adopted. To facilitate the growth of the graded transition regions as narrow as a few hundred Angstrom units, the overall growth rate was kept low, at  $0.25\mu\text{m/hr}$ . During the growth of the GaAs layers, the indium furnace was kept idling at a reduced temperature that would correspond to a very low growth rate of about  $25\text{\AA/hr}$ , but with the shutter closed. The growth of the transition layer was initiated by re-setting the indium furnace controller setpoint to the full  $0.25\mu\text{m/hr}$  growth rate, and opening the shutter. After an additional 3min delay, the gallium furnace controller was reset to a  $500^\circ\text{C}$  idle

temperature, and that furnace was simply allowed to cool. This caused the Ga flux to drop to approximately 1% of its initial value within about 8min. The overall thickness of the graded layer is estimated to be about 400Å. The contact resistivity of such (Ga,In)As graded layers was estimated in a separate experiment to be about  $3 \times 10^{-7} \Omega\text{cm}^2$  [4].

The sample was removed from the MBE system and approximately 1500Å of SiO<sub>2</sub> was deposited by plasma assisted chemical vapor deposition. The SiO<sub>2</sub> was patterned with HF into the emitter regions using conventional photoresist processing techniques. The photoresist was removed, the sample ashed in an O<sub>2</sub> plasma, and emitter mesas were etched. The sample was then loaded back into the MBE system for regrowth. Approximately 1000Å of p<sup>+</sup>-GaAs, followed by 350Å of graded Ga(As,Sb) were grown. The sample was removed from the MBE system, base mesas etched, and the regrown layer on top of the SiO<sub>2</sub> was removed by dissolving the SiO<sub>2</sub> in HF.

At this point the devices were probed using tungsten probe tips *directly* contacting the semiconductor surfaces of the base and emitter. The probes were found to make ohmic contact to



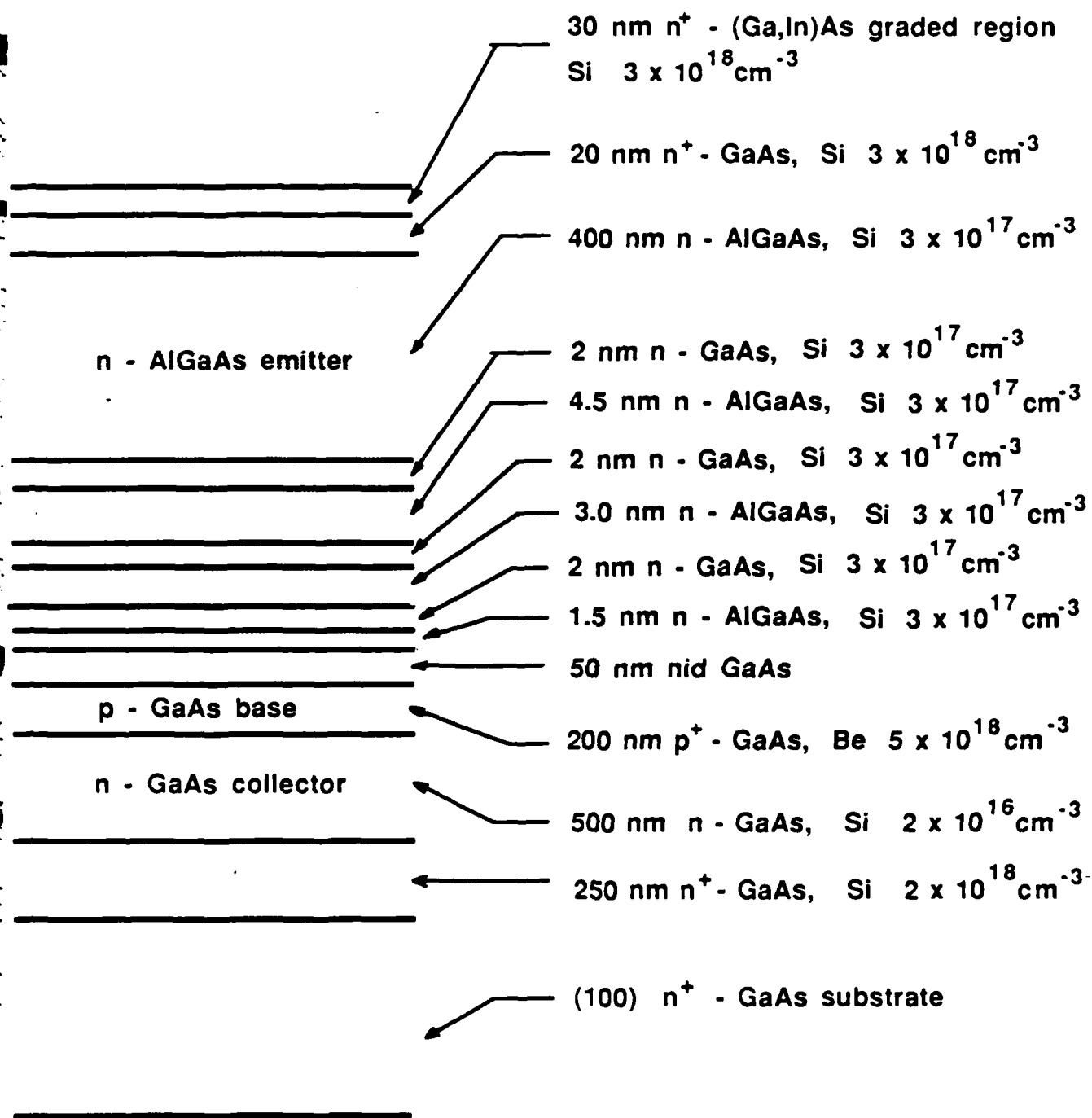


Fig. 4.1  $\text{Al}_x\text{Ga}_{1-x}\text{As} / \text{GaAs}$  HBT layer diagram. The value of  $x$  is 0.15.  
Vertical dimensions are not to scale.

the base and the emitter. Indium alloyed into the  $n^+$ -substrate formed the collector contact. The device I/V characteristics are shown in Fig. 4.2. Dc current gains of 20 were obtained at collector current densities of  $200 \text{ A/cm}^2$ . The low current gains are attributed to low Al fraction of 0.15 in the (Al,Ga)As emitter, and the non-optimized digitally graded emitter grown for the first time in this laboratory. In addition, evaporated metal (non-alloyed) contacts on the base and emitter regions will reduce spreading resistance and will allow for a dual base contact.

Aluminium was used for the final metallization, and  $\text{SiO}_2$  was used as the insulator. After the final metallization step the base-collector junctions were found to be very leaky. We believe that this leakage is surface leakage, probably due to a Si-rich  $\text{SiO}_2$ . We intend to use polyimide as a dielectric layer on subsequent runs.

#### 4.2 ACKNOWLEDGEMENTS

We would like to thank Dr. E. J. Caine and Messrs. A. Yuen, S. Subbanna and R. Simes for useful discussions.

#### 4.3 REFERENCES

- [1] S. L. Su, R. Fischer, W. G. Lyons, O. Tejayadi, D. Arnold, J. Klem, and H. Morkoc, "Double heterojunction GaAs/ $\text{Al}_x\text{Ga}_{1-x}$ As bipolar transistors prepared by molecular beam epitaxy," J. Appl. Phys., **54** (11), 6725 (1983).
- [2] R. J. Malik, F. Capasso, R. A. Stall, R. A. Kiehl, R. W. Ryan, R. Wunder, and C. G. Bethea, "High-gain, high-frequency AlGaAs/GaAs graded band-gap base bipolar transistors with a Be diffusion setback layer in the base," Appl. Phys. Lett., **46** (6), 600 (1985).
- [3] B. R. Hancock, "Development of inverted (Al,Ga)As heterojunction bipolar transistors by molecular beam epitaxy," Ph.D. dissertation, Dept. Electrical and Computer Engineering, Univ. Calif. Santa Barbara, 1985.
- [4] E.J. Caine and H. Kroemer, "Non-alloyed graded-gap (Ga,In)As ohmic contacts to GaAs and their use in GaAs MESFETs," submitted for publication to the IEEE Electron Device Letters.

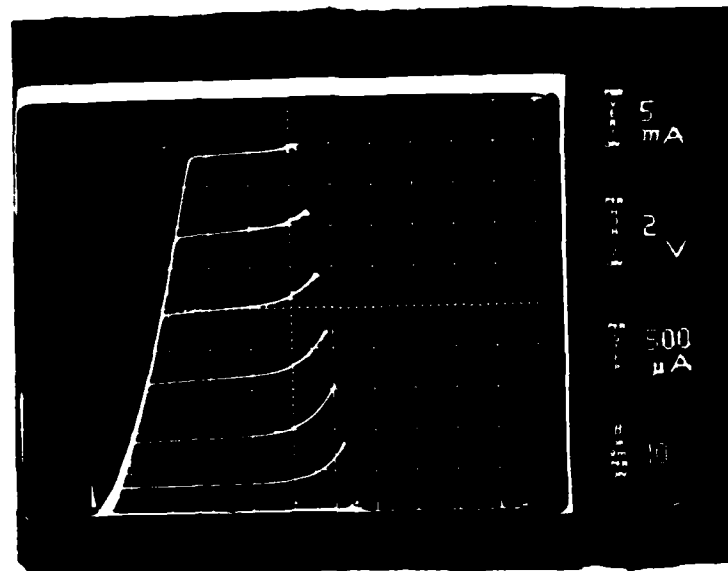


Fig. 4.2  $I_C/V_{CE}$  curves for the HBT with graded-gap ohmic contacts for both the emitter and the base. The curves were obtained before the final metallization using tungsten probes to form ohmic contacts to the base and the emitter.

## 5. PERSONNEL

Professor Stephen I. Long is the Principal Investigator and Professor Herbert Kroemer is the Co-principal Investigator. Graduate Research Assistants, B. Hancock and M. Rao, are supported by, and are the main student contributors to, this effort. Mr. Hancock completed his Ph.D. dissertation entitled "Development of Inverted (Al,Ga)As Heterojunction Bipolar Transistors by Molecular Epitaxy," which was delivered to AFOSR as a separate report in October, 1985. Mr. Rao completed work on InGaP/GaAs heterojunction, and is preparing an M.S. thesis on this topic. He is continuing research on the graded gap ohmic contacts and HBTs.

## 6. PUBLICATIONS AND PRESENTATIONS

- [1] M.A. Rao, E.J. Caine, H. Kroemer and S.I. Long, "Determination of valence and conduction band discontinuities at the (Ga,In)P/GaAs heterojunction by C-V profiling," submitted for publication to the Journal of Applied Physics.
- [2] M.A. Rao, E.J. Caine, S.I. Long and H. Kroemer, "AlGaAs/GaAs heterostructure bipolar transistor with non-alloyed graded-gap ohmic contacts to the base and emitter," to be presented at the 1986 Device Research Conference, Amherst, MA, June, 1986.

**Determination of valence and conduction band discontinuities  
at the (Ga,In)P/GaAs heterojunction by C-V profiling**

M. A. Rao, E. J. Caine, H. Kroemer, S. I. Long, and D. I. Babic <sup>a)</sup>

Department of Electrical and Computer Engineering

University of California, Santa Barbara, California 93106.

**ABSTRACT**

The valence and conduction band discontinuities for the lattice matched (Ga,In)P/GaAs heterojunction have been determined by C-V profiling. The band lineup is found to be of the straddling type with the valence and conduction band discontinuities 0.25 eV and 0.21 eV, respectively. Computer reconstruction of the C-V profiles was used to check the consistency of the data. The band offset data indicate that the (Ga,In)P/(Al,Ga)As system should be staggered for a certain range of Al composition.

<sup>a)</sup> Now at Avantek Inc., Santa Clara, CA 95051

the original work by Kroemer et al. [4], and more recently by Watanabe et al. [8], but not in the other papers on the determination of band offsets by C-V profiling [5-7]. In the present work, computer reconstruction formed an essential part of the analysis.

## II. SAMPLE PREPARATION

### A. Sample Structures

Epitaxial layers of (Ga,In)P and GaAs were grown by molecular beam epitaxy in a Varian-360 MBE machine, on (100)-oriented, Si-doped  $n^+$  GaAs substrates. Both n-n and p-p isotype structures were grown, for separate  $\Delta E_c$  and  $\Delta E_v$  measurements. The overall structures, with the thicknesses and doping levels of the layers, were as shown in Fig. 1. With the n-n structures, the profiling was conducted from a reverse-biased aluminum Schottky barrier deposited on the n-(Ga,In)P surface (Fig. 1a). Because Schottky barriers on p-(Ga,In)P were too leaky to permit C-V profiling, the profiling of the p-p heterojunctions (HJs) was carried out by continuing to use an  $n^+$  substrate, and profiling upward from the reverse-biased  $n^+$ -p junction between the substrate and the p-GaAs epi-layer (Fig. 1b). The schematic energy band diagrams of the HJ portion of the two structures are shown in Fig. 2, both oriented such that the profiling direction is from the left to the right.

### B. Growth Procedure

The GaAs substrates were cleaned in organic solvents, and etched in room-temperature  $\text{NH}_4\text{OH} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 2 : 1 : 20$  for two minutes. This was followed by a 10 min rinse in de-ionized water to form a native oxide. The oxide was desorbed by heating inside the MBE system in the presence of an

### C. Preparation of samples for C-V profiling

On the n-n samples, aluminum Schottky diodes were fabricated by deposition and lift-off. The diode area was  $4.8 \times 10^{-4} \text{ cm}^2$ . On the p-p samples, Au-Zn dots were deposited by evaporation and lift-off, and alloyed at  $450^\circ\text{C}$  for 30 sec on a graphite strip heater, to form an ohmic contact to the p-(Ga,In)P. Diode mesas were then formed by etching the (Ga,In)P with  $\text{HCl} : \text{H}_3\text{PO}_4 = 1 : 1$ . We found that this etchant produced less undercutting than the undiluted HCl etch commonly used for etching (Ga,In)P. Following the (Ga,In)P etch, the p-GaAs was etched with  $\text{H}_3\text{PO}_4 : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 5 : 1 : 14$ , to a depth sufficient to reach into the  $n^+$  substrate. The final p-p diode mesa area was measured to be  $4.6 \times 10^{-4} \text{ cm}^2$ . The return contact for both n-n and p-p structures was formed by indium alloyed to the  $n^+$  substrate.

## III. C-V PROFILING: RESULTS AND DISCUSSION

Because we found the p-p results more trustworthy, they are discussed first.

### A. $\Delta E_v$ measurements

As stated earlier, the C-V profile through the p-(Ga,In)P/p-GaAs HJ was obtained by reverse biasing the  $n^+$ -p junction between the substrate and the p-GaAs epi-layer, shown in Fig. 1b. A HP4280A C-V meter was used for the measurement. The measurement frequency was 1MHz, and the magnitude of the applied differential voltage was 30 mV (rms). The apparent majority carrier concentration profile  $\hat{p}(x)$  was derived from the C-V profile according to the standard relation

$$\hat{p}(x) = \frac{2}{q\epsilon} \left[ \frac{d}{dV} \left[ \frac{1}{C^2} \right] \right]. \quad (1)$$

$P(x)$  : doping profile, assumed to be known and to level out far away from the HJ;

$P_{1,2}$  : asymptotic values of the doping levels in the GaAs (\*1) and the (GaIn)P (\*2);

$x_i$  : distance of the HJ interface from the  $n^+$ -p junction;

$N_{v1,2}$  : valence band density of states in the two regions.

An accurate determination of  $P_1$  and  $P_2$  is necessary if the band discontinuity is to be obtained with confidence. It can be seen from the  $\hat{p}(x)$  curve that the hole concentrations on both sides of the HJ leveled out very well; thus  $P_1$  and  $P_2$  could be accurately established.

Our model used to reconstruct the C-V profile assumes an abrupt HJ with a step change in the doping on the two sides, as well as the existence of a localized interface defect charge  $\sigma_i$ . The value of  $\sigma_i$  is obtained from the requirement of overall charge neutrality [4] :

$$\sigma_i = \int_0^{\infty} [\hat{p}(x) - P(x)] dx \quad (4)$$

In such a model an accurate knowledge of the interface position  $x_i$  is essential. Although a nominal value for the thickness of the GaAs layer was known from the growth rate, the accuracy of this value was not sufficient for use in determining  $\Delta E_v$ . A series of values of  $\Delta E_v$  and of the interface charge density  $\sigma_i$  were therefore calculated from (3) and (4), for a series of *assumed* values of the interface position  $x_i$  around the nominal value (Fig. 4). The values of  $\Delta E_v$  and  $\sigma_i$ , for each assumed  $x_i$ , were next used to reconstruct numerically the apparent carrier concentration profile, using a



computer program that basically solves Poisson's equation for incremental voltage steps applied at the HJ [12]. The experimental and reconstructed profiles were compared for each of the assumed  $x_i$  values, and  $x_i$  varied until a "best" fit was obtained. While we had no quantitative criteria for judging the closeness of the fit, we found that the best overall agreement between the experimental and reconstructed profile occurred for interface positions that also yielded small values of interface charge.

It is evident from Fig. 4 that the valence band offset  $\Delta E_v$  exhibits a broad minimum around that  $x_i$ -value that corresponds to zero interface charge. This is a general property of the model: It is not difficult to prove that an extremum of the band offset (a maximum or minimum, depending on the signs of the band offset and of the doping step) occurs *necessarily* at that  $x_i$ -value for which the interface charge vanishes. For HJs with a low *true* interface charges, this behavior has the highly desirable consequence that the calculated band offset value is a relatively insensitive function of the assumed interface location.

For our p-p junction the best overall agreement was obtained for  $x_i = 0.555 \mu\text{m}$ , yielding  $\Delta E_v = 0.239 \text{ eV}$ ,  $\sigma_i = +3.68 \times 10^{10} \text{ cm}^{-2}$ , near the band offset minimum in Fig. 4, but not exactly at it. The reconstructed profile itself is shown in Fig. 3. It can be seen that the agreement between the experimental and reconstructed profiles, although far from perfect, is quite good. The remaining discrepancies must be viewed as indications that our model of a perfectly abrupt interface is not fully applicable, but it is difficult to say more. Expressed as a fraction of the total energy gap difference,  $\Delta E_g \approx 0.459 \text{ eV}$  [13], our  $\Delta E_v$ -value corresponds to  $0.52 \Delta E_g$ .

Our experimental value is about 50 meV smaller than the theoretical prediction [1] of  $\Delta E_v \approx 0.29 \text{ eV} \approx 0.65 \Delta E_g$  for the lattice-matched  $\text{Ga}_{0.51}\text{In}_{0.49}\text{P}/\text{GaAs}$  interface, obtained by simple linear interpolation between the theoretical valence band offsets for  $\text{GaP}/\text{GaAs}$  and  $\text{InP}/\text{GaAs}$  that are predicted by the Harrison theory [3]. Although by no means negligible, this discrepancy is actually smaller than the discrepancy for most hetero-systems.

### B. $\Delta E_c$ measurements

The structure shown in Fig. 1(a) was used to measure  $\Delta E_c$ . The aluminum Schottky barrier was reverse-biased to obtain a C-V profile through the HJ. The analysis of the data was analogous to that for the p-p structure. Fig. 5 shows the experimental carrier concentration profile, in which electron accumulation and depletion can be seen in the GaAs and (Ga,In)P, again as expected from the predicted energy band diagram shown in Fig. 2a. Fig. 6 shows a graph of  $\Delta E_c$  and  $\sigma_i$  as a function of  $x_i$ .

We were not able to obtain as good a fit between experimental and reconstructed carrier concentration profiles as for the p-p case. The reconstructed profile shown in Fig. 5 represents the "least bad" fit, corresponding to the triplet  $x_i = 0.500 \mu\text{m}$ ,  $\Delta E_c = 0.189 \text{ eV}$ ,  $\sigma_i = -1.6 \times 10^{10} \text{ cm}^{-2}$ . Again this profile is one with a small interface charge, and again the value of the band offset is not very sensitive to the choice of  $x_i$ . Note that the band offset extremum is this time a maximum.

The peak-to-valley concentration ratio of the experimental profile is lower, and the peak and valley are separated farther in space than in the reconstructed profile. This combination indicates that either the energy gap

or the doping profile of the actual junction must be graded at the transition, in contrast to the mathematical model used in the reconstruction, which assumed an abrupt transition at the interface for both.

The difference between the two kinds of gradients is important for the determination of the band offset: As was shown by Kroemer [9], in the presence of a purely compositional (energy gap) gradient at the HJ, not accompanied by a doping gradient, the electrostatic dipole moment associated with the broadened  $\hat{n}(x)$  curve remains unchanged, and the relation (3) -- or its n-n equivalent -- still yields the correct (abrupt-limit) value of  $\Delta E_C$ , even though the reconstruction with an abrupt mathematical model fails. On the other hand, if the doping profile is graded, this changes the dipole moment, and hence the band offset.

A sputter-Auger analysis of our sample, which would have been able to detect any compositional grading on the scale required by the discrepancy between the two curves in Fig. 5, showed no significant compositional grading near the HJ. We therefore believe that in our case the grading is due to a doping gradient rather than a compositional gradient. We suspect that the postulated doping gradient is due to strain-induced diffusion: Studies of masked diffusion in GaAs [14] have shown the presence of large lateral diffusion of the diffusant in the presence of strain at the mask/GaAs interface. In those studies the masks were deposited films of silica, phosphosilicate glass, or silicon nitride, and the strain at the mask/GaAs interface was caused due to their different thermal expansion characteristics. In our n-n sample, significant outdiffusion of Si could have taken place at the GaAs/(Ga,In)P interface, due to strain caused by the non-negligible residual lattice mismatch in that sample. In contrast, it

should be recalled that the p-p isotype interface was relatively strain-free.

If one inspects the n-n equivalent of (3) for our case of a heavier doping on the GaAs side, one finds readily that the presence of a doping gradient at the interface causes an *increase* in the value of  $\Delta E_C$  relative to the abrupt-model value. To estimate the correction, at least to a first order, the doping gradient may be approximated by a straight line extending over a distance equal to that between the accumulation and depletion extrema in the experimental profile, as shown in Fig. 7. The contribution of the grading to the electrostatic dipole moment is then simply that of the two shaded triangles. This moment is estimated to be 0.024 eV, and the true  $\Delta E_C$  should be higher by this amount, yielding a corrected conduction band offset of  $\Delta E_C \approx 0.213 \text{ eV} \approx 0.46 \Delta E_g$ . The value of  $\Delta E_C$  predicted from the Harrison model was  $0.160 \text{ eV} \approx 0.35 \Delta E_g$ .

Our two independent experimental band offsets add up to  $\Delta E_V + \Delta E_C = 0.452 \text{ eV}$ , within less than 2% of the experimental value of the energy gap difference,  $\Delta E_g = 0.459 \text{ eV}$ , suggesting that the individual values should be quite trustworthy. The remaining discrepancy of 7 meV probably reflects some combination of a small amount of doping grading at the p-p interface, or inaccuracies in our rather crude accounting for the grading at the n-n interface. Inasmuch as our reconstruction fit for the p-p junction is distinctly less than perfect, we tentatively assign the discrepancy to the valence band offset, implying an adjusted value  $\Delta E_V \approx 0.246 \text{ eV} \approx 0.54 \Delta E_g$ .

#### IV. CONCLUSIONS

The valence and conduction band edge discontinuities for (Ga,In)P lattice-matched to GaAs have been determined by C-V profiling. As

expected, the band lineup between (Ga,In)P and GaAs is of the straddling type. Reasonable agreement between the experimental and reconstructed profiles was obtained for the p-p isotype structure, and the valence band discontinuity was obtained to be 0.25 eV, or  $0.54 \Delta E_g$ . Comparison of the experimental and reconstructed profiles for the n-n isotype structure indicated the presence of significant grading at the interface. A first-order correction of the raw data to the measured  $\Delta E_C$  was estimated, yielding a corrected value of  $\Delta E_C$  of 0.21 eV, or  $0.46 \Delta E_g$ . The values of  $\Delta E_V$  and  $\Delta E_C$ , obtained from independent measurements, add up to 98% of  $\Delta E_g$ , indicating good self-consistency, and suggesting an accuracy of the individual values themselves to probably better than  $\pm 10$  meV.

Our demonstration that the band lineup is of the straddling type refutes the interpretation, by Hsieh et al. [15], of their below-gap photoresponse data of (Ga,In)P/GaAs heterojunctions, in terms of a staggered lineup. In fact, we find the interpretation of these data in terms of a staggered lineup forced and unconvincing in its own right, even if there were no conflicting lineup data.

Our lineup data lead to interesting predictions for the band lineups for (Ga,In)P lattice-matched to  $Al_xGa_{1-x}As$ . In Fig. 8, taken from a recent review [16], we have superimposed our conduction and valence band edge energy values for (Ga,In)P on current "best estimate values" for the lineups *within* the  $Al_xGa_{1-x}As$  alloy system [16]. It appears that the valence band of  $Al_xGa_{1-x}As$  will drop below that of lattice-matched (Ga,In)P for  $x > 0.49$ . The conduction band offsets are more complicated, due to the  $\Gamma$  - to - X crossover in the  $Al_xGa_{1-x}As$  band structure around  $x = 0.43$ . We estimate that the conduction band of  $Al_xGa_{1-x}As$  will initially rise above that of (Ga,In)P for  $x > 0.26$ . For  $x > 0.43$ , the conduction band energy of  $Al_xGa_{1-x}As$  drops

again, and it should reach a value very close to the (Ga,In)P value as  $x \rightarrow 1.0$ . Thus there are likely to be three  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  composition ranges with quite different behavior: (i) For  $x < 0.26$ , the band lineup should remain a straddling one, with  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  retaining the lower total gap, and with a vanishing conduction band offset at the upper end of this range. (ii) For  $0.26 < x < 0.49$ , the system should be a staggered one, with (Ga,In)P having both bands below those of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ . The residual interface gap should slowly increase through this range, from about 1.77 eV for  $x = 0.26$  to 1.95 eV for  $x = 0.49$ . This might be an interesting range for the study of staggered-lineup luminescence [17],[18] in p- $\text{Al}_x\text{Ga}_{1-x}\text{As}$ /n-(Ga,In)P heterojunctions. (iii) For  $x > 0.49$ , the band lineup would become straggling again, but now with (Ga,In)P having the smaller energy gap.

It would appear that these band lineups might find applications in future electronic and optoelectronic device structures. With regard to the initial motivation for this work, the use of (Ga,In)P/GaAs HJs as emitters in HBTs, both our data and the recent re-assessments of the band lineups within the  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  alloy system [16] diminish somewhat the attractiveness of that idea: The conduction band offsets in the (Ga,In)P/GaAs system are not quite as small as had been hoped, and those within the  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  alloy system are not as large as had been feared. Together with the more difficult technology of (Ga,In)P relative to (Al,Ga)As, these changes conspire to reduce the incentive for (Ga,In)P as a material for HBTs, but probably not for other applications.

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## REFERENCES

- [1] H. Kroemer, J. Vac. Sci. Technol. **B1**, 126 (1983).
- [2] M. J. Mondry and H. Kroemer, IEEE Electron Dev. Lett. **EDL-6**, 175 (1985).
- [3] W. A. Harrison, J. Vac. Sci. Technol. **14**, 1016 (1977).
- [4] H. Kroemer, W. Y. Chien, J. S. Harris, Jr., and D. D. Edwall, Appl. Phys. Lett. **36**, 295 (1980).
- [5] R. People, K. W. Wecht, K. Alavi and A. Y. Cho, Appl. Phys. Lett. **43** 118 (1983).
- [6] M. Ogura, M. Mizuta, K. Onaka, and H. Kukimoto, Jpn. J. Appl. Phys. **22**, 1502 (1983).
- [7] S. R. Forrest, P. H. Smith, R. B. Wilson, and M. L. Kaplan, Appl. Phys. Lett. **45**, 1190 (1984).
- [8] M. O. Watanabe, J. Yoshida, M. Mashita, T. Nakanisi, and A. Hojo, J. Appl. Phys. **57**, 5340 (1985).
- [9] H. Kroemer, Appl. Phys. Lett. **46**, 504 (1985).
- [10] M. J. Mondry, E. J. Caine, and H. Kroemer, J. Vac. Sci. Technol. **A3**, 316 (1985). See also S. L. Wright and H. Kroemer, J. Vac. Sci. Technol. **20**, 143 (1982).
- [11] The value of  $\epsilon$ , and its position dependence, cancel out in the final value of the band offsets; see D. Babic and H. Kroemer, Solid-State Electron. **28**, 1015 (1985).
- [12] D. I. Babic., M.S. Dissertation, ECE Dept., Univ. Calif. Santa Barbara, 1984, unpublished.
- [13] H. C. Casey, Jr. and M. B. Panish, *Heterostructure Lasers Part B: Materials and Operating Characteristics* ( Academic, New York, 1978), see Table 5.3-1.
- [14] B. J. Baliga and S. K. Gandhi, IEEE Trans. Electron Dev. **TED-21**, 410



- (1974).
- [15] S. J. Hsieh, E. A. Patten, and C. M. Wolfe, Appl. Phys. Lett. **45**, 1125 (1984).
- [16] For a review containing extensive references to the original workers, see H. Kroemer, Proc. 2nd Int. Conf. Modulated Semicond. Structures, (MSS-II), Kyoto, 1985; Surf. Sci., in print.
- [17] H. Kroemer and G. Griffiths, IEEE Electron Dev. Lett. **EDL-4**, 20 (1983).
- [18] E. J. Caine, S. Subbanna, H. Kroemer, J. L. Merz, and A. Y. Cho, Appl. Phys. Lett. **45**, 1123 (1984).

## FIGURE CAPTIONS

- Fig. 1 Structure of samples for C-V Profiling: (a) Sample for determination of conduction band offset by profiling through an n-n junction from a surface Schottky barrier; (b) Sample for determination of valence band offset by profiling through a p-p junction from a buried  $n^+$ -p junction.
- Fig. 2 Expected band diagrams (a) for the n-n heterojunction; (b) for the p-p heterojunction. Both are oriented such that the profiling direction is from the left to the right.
- Fig. 3 Experimental and reconstructed apparent carrier concentration profiles for the p-p structure.
- Fig. 4 Plot of  $\Delta E_v$  and  $\sigma_i$  for the p-p heterojunction, as a function of assumed interface position  $x_i$ .
- Fig. 5 Experimental and reconstructed apparent carrier concentration profiles for the n-n structure.
- Fig. 6 Graph of  $\Delta E_c$  and  $\sigma_i$  for the n-n heterojunction as a function of assumed interface position  $x_i$ .
- Fig. 7 Simple model for the doping gradient postulated to be present in the n-n heterojunction.
- Fig. 8 Predicted relative band edge energies at (Ga,In)P/(Al,Ga)As. The heavy solid lines represents the band edge energies in the alloy system, relative to straight GaAs, as a function of  $x$ , taken from ref. [16]. The horizontal broken lines represents the (Ga,In)P band energies relative to GaAs, for (Ga,In)P lattice-matched to straight GaAs, as determined in the present work.

FIG. 1

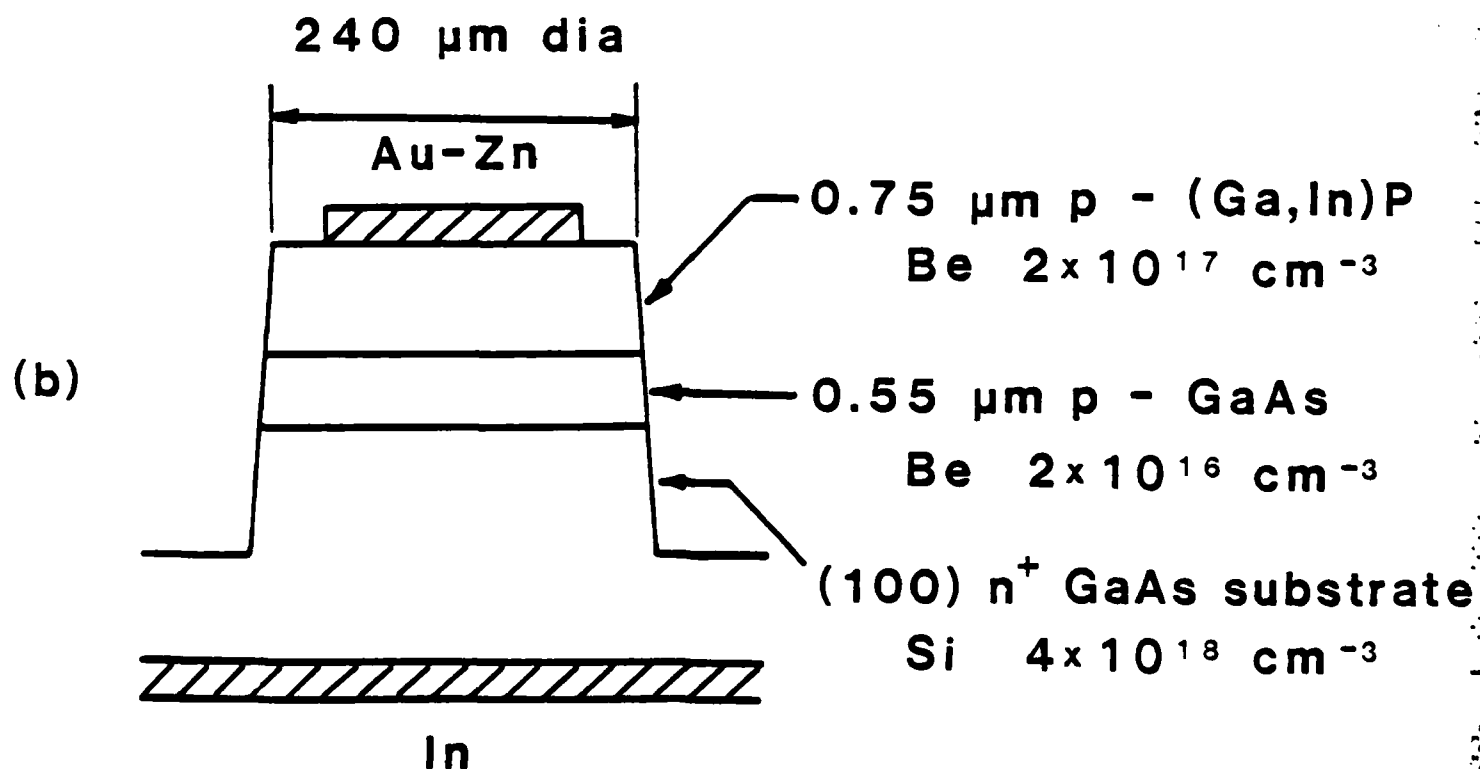
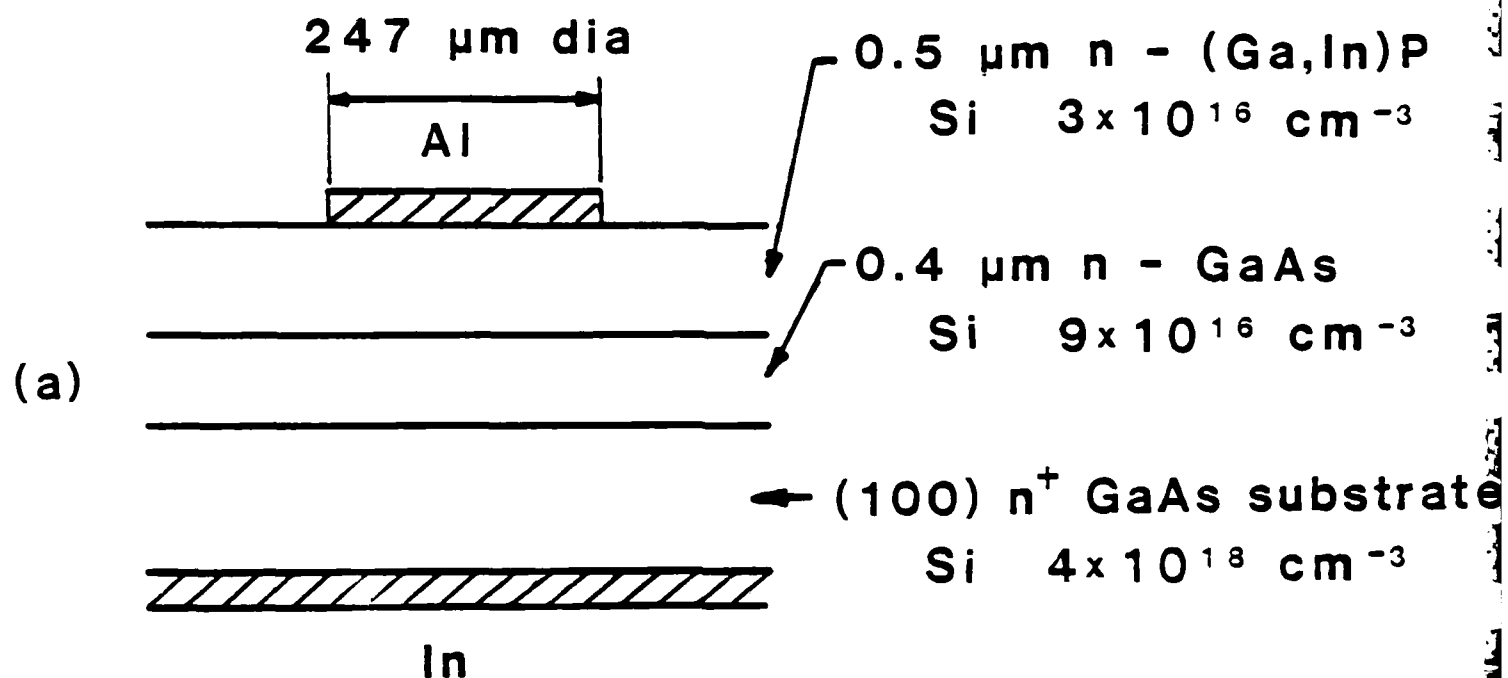


FIG. 2

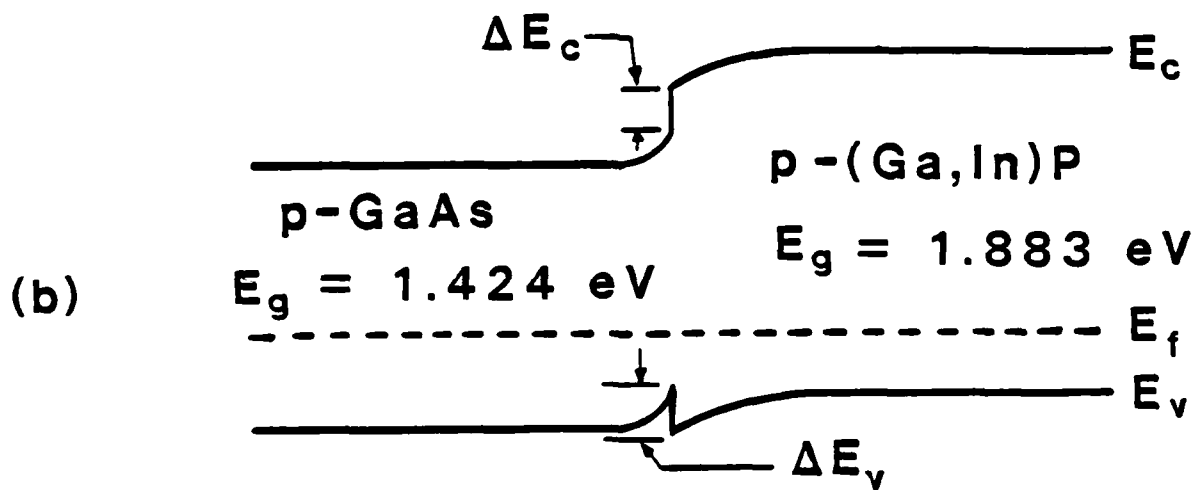
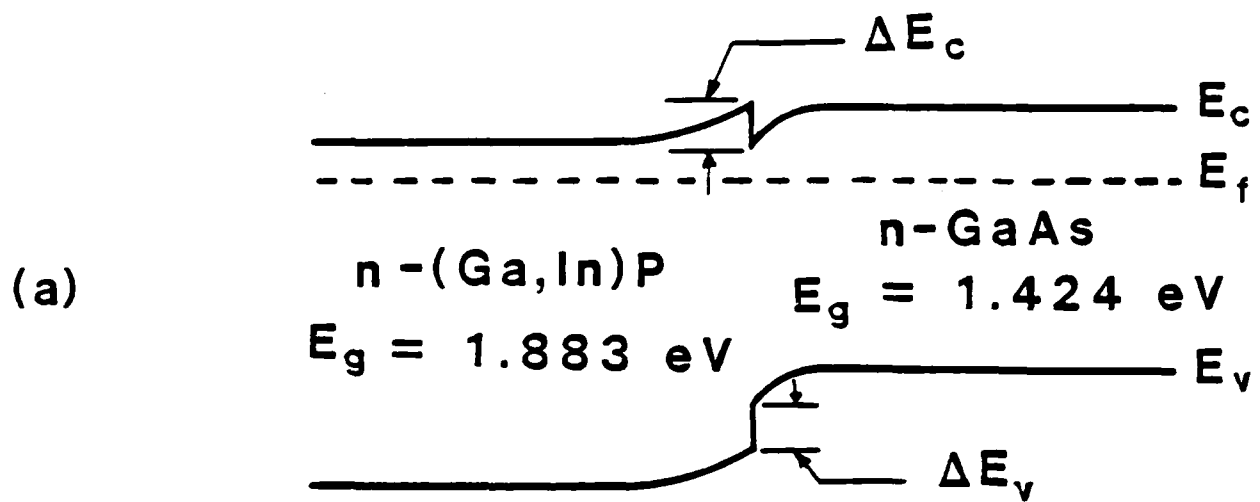


FIG. 3

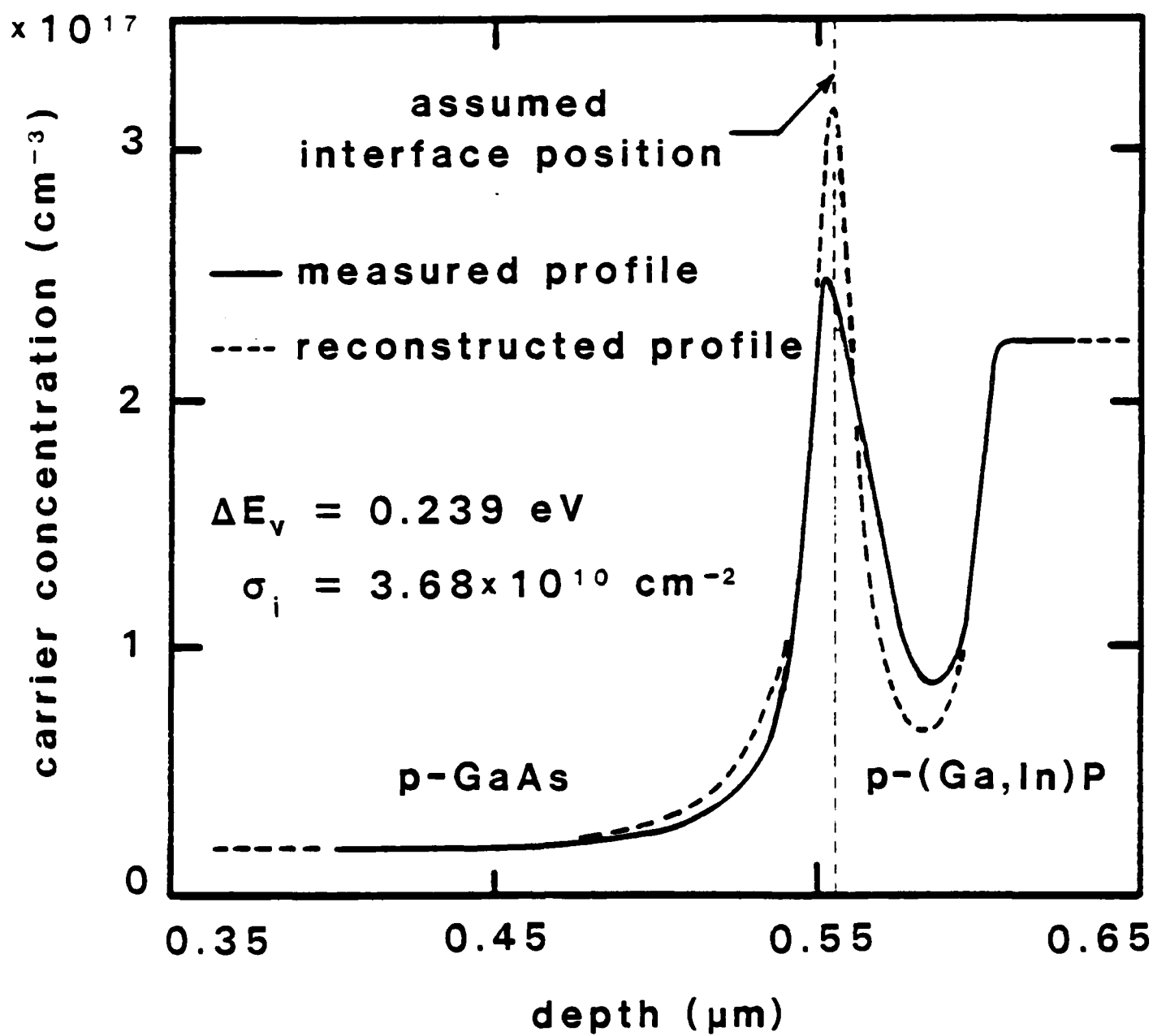


FIG. 4

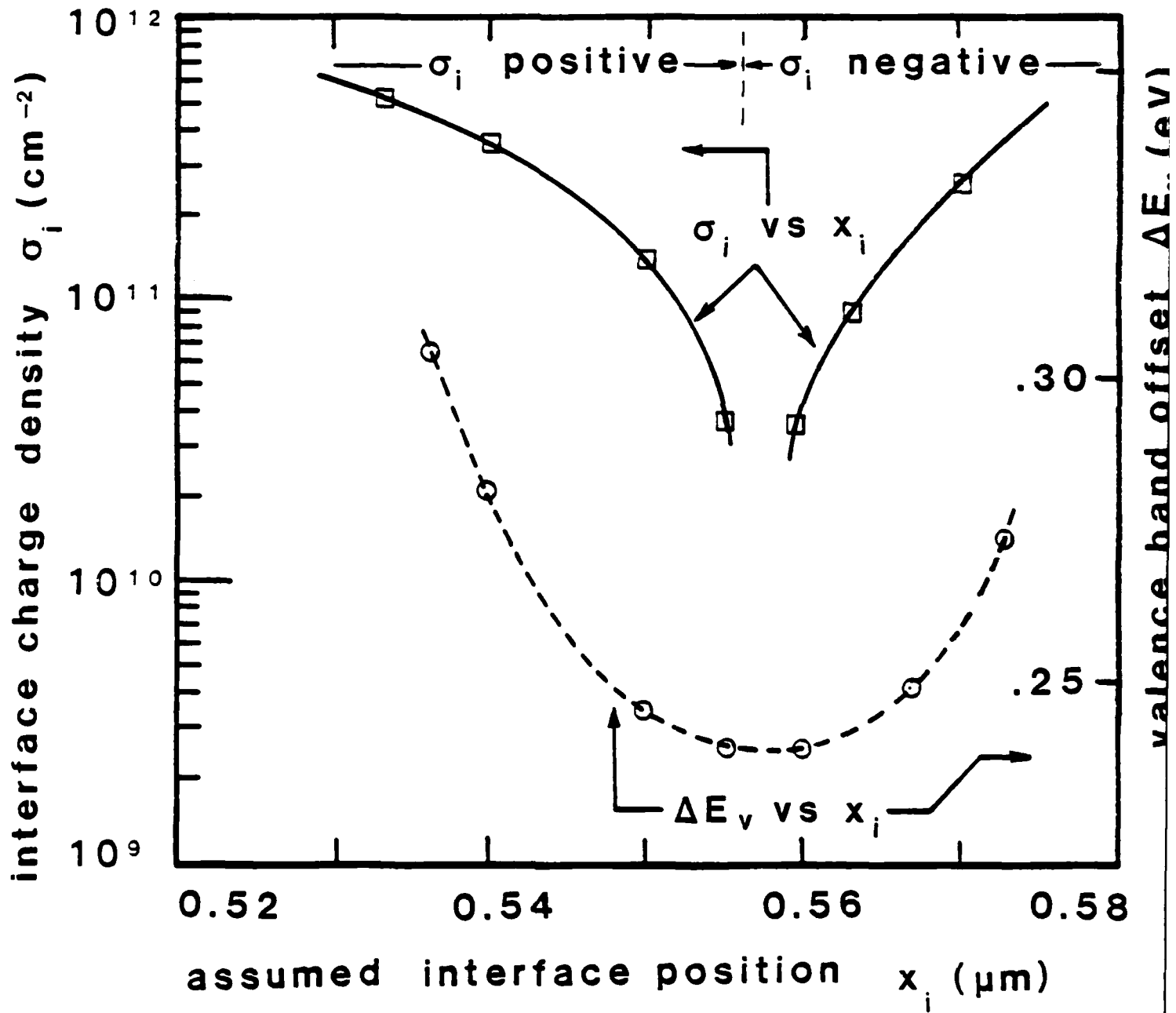


FIG. 5

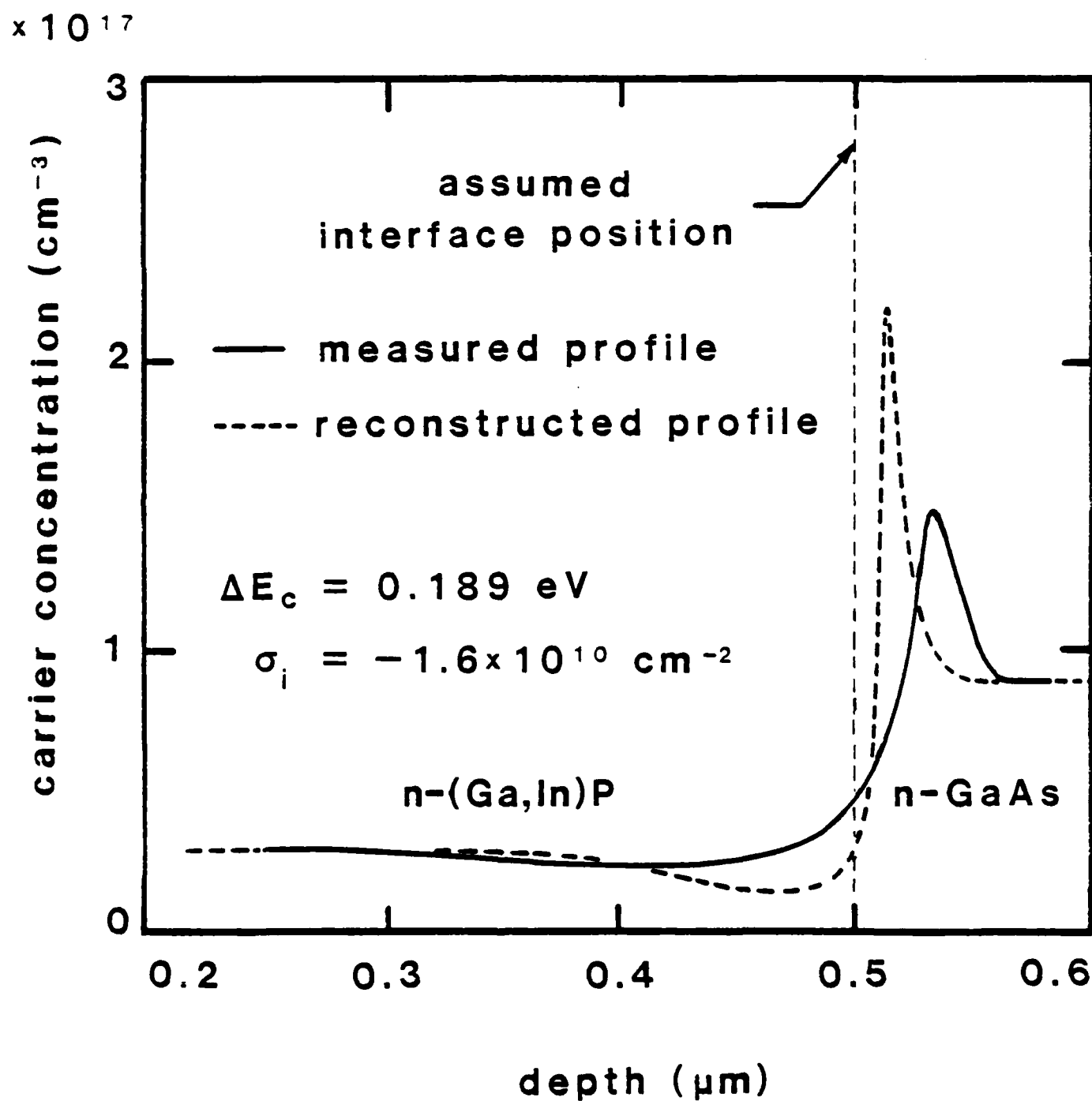


FIG. 6

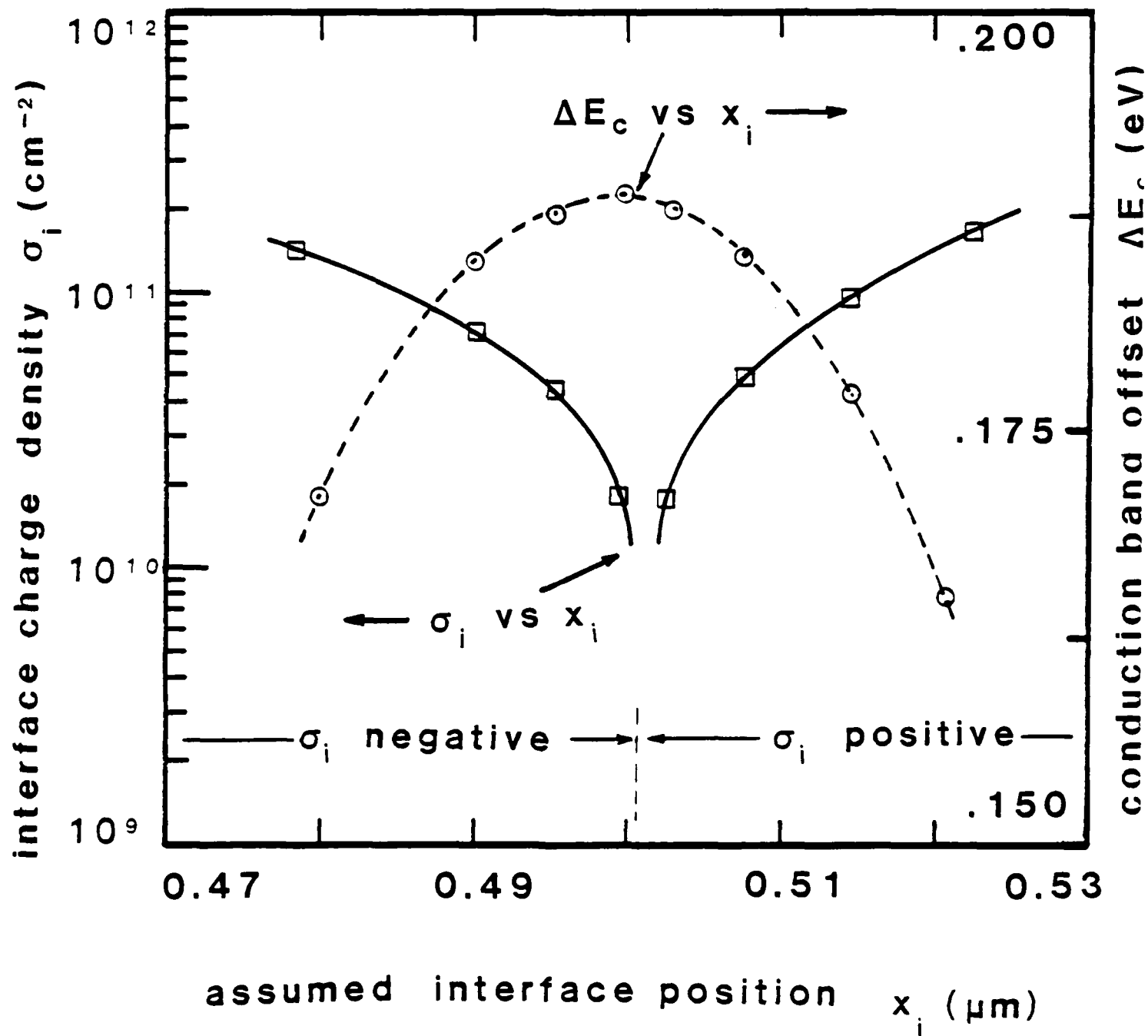




FIG. 7

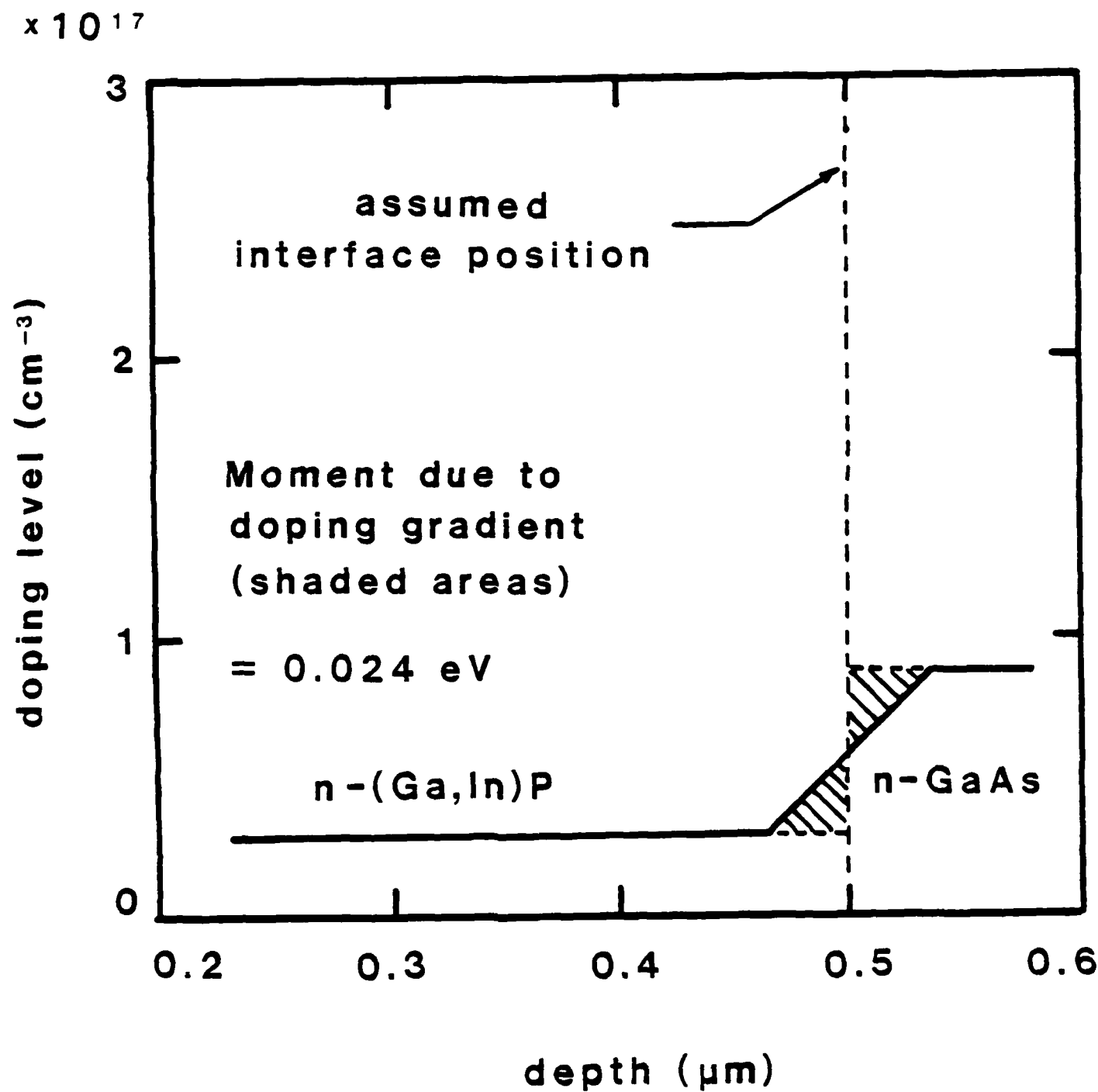
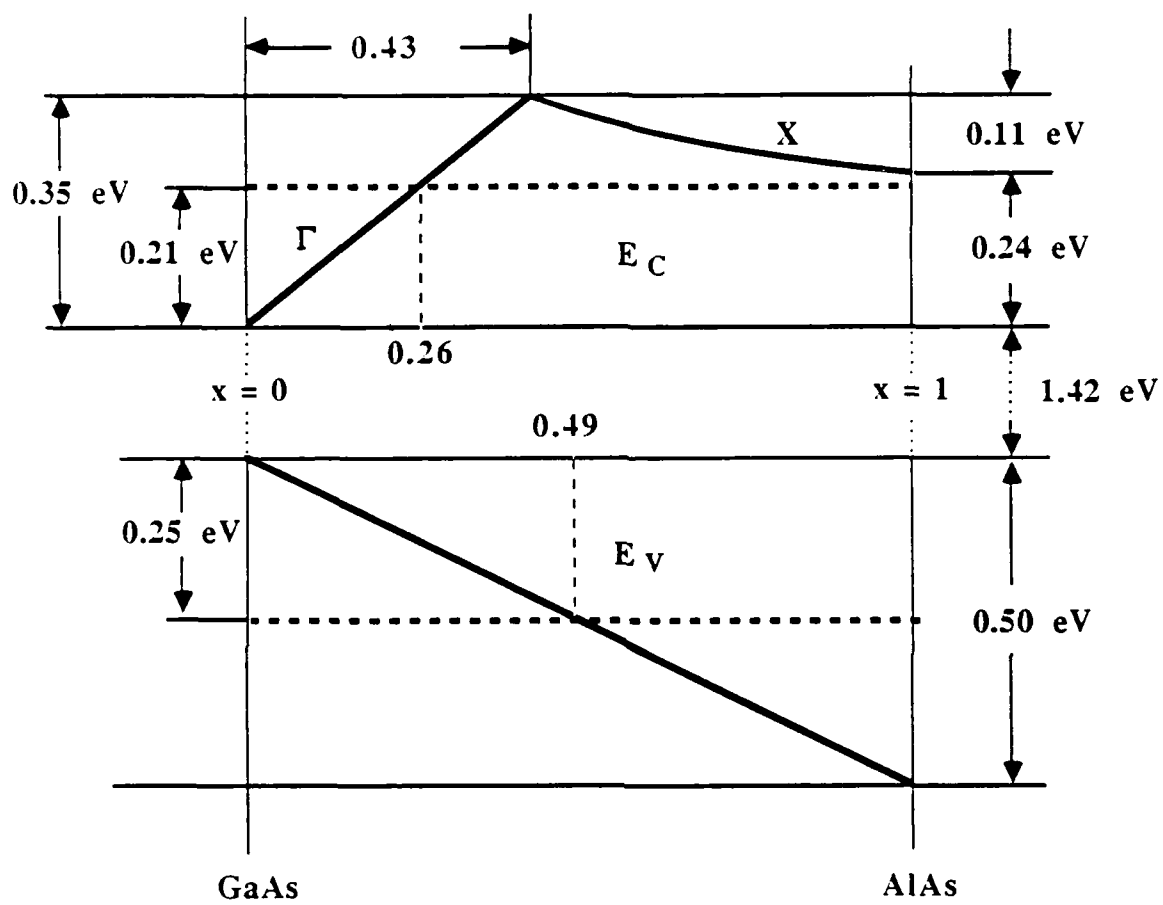


FIG. 8



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